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<p>(21) International Application Number: PCT/EP93/00989 (22) International Filing Date: 23 April 1993 (23.04.93) (30) Priority data: 92107137.9 27 April 1992 (27.04.92) EP (34) Countries for which the regional or international application was filed: DE et al. (71) Applicant (for all designated States except US): MERCK PATENT GMBH [DE/DE]; Frankfurter Straße 250, Postfach 4119, D-6100 Darmstadt (DE). (72) Inventors; and (75) Inventors/Applicants (for US only): COATES, David [GB/GB]; 87 Sopwith Crescent, Merley, Wimborne, Dorset BH12 3SW (GB). PARRI, Owain, Llyr [GB/GB]; 45 Houlton Road, Poole, Dorset BH15 2LN (GB). GREENFIELD, Simon [GB/GB]; 2 Blackbird Close, Creekmoor, Poole BH17 7YA (GB). TILLIN, Martin, David [GB/GB]; Flat 1, 7 Eldon Place, Westbourne, Bournemouth, Dorset BH4 9AZ (GB). GOULDING, Mark, John [GB/GB]; Flat 3, 20 Durrant Road, Lower Parkstone, Poole BH14 8TP (GB). NOLAN, Patrick [GB/GB]; 16 Colbourne Close, Baiter Park, Poole BH15 1UF (GB).</p>		<p>(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.</p>
<p>(54) Title: ELECTROOPTICAL LIQUID CRYSTAL SYSTEM</p> <div style="text-align: center; margin: 20px 0;"> <p style="text-align: right;">(I)</p> </div> <div style="text-align: center; margin: 20px 0;"> <p>(a)</p> </div> <div style="text-align: center; margin: 20px 0;"> <p>(b)</p> </div> <p>(57) Abstract</p> <p>Electrooptical system with improved switching time especially at low temperatures: which between 2 electrode layers contains a PDLC film comprising a liquid crystal mixture forming microdroplets in an optically isotropic, transparent polymer matrix, the precursor of the PDLC film comprises one or more monomers, oligomers and/or prepolymers and a photoinitiator, and is cured photoradically, the liquid crystal mixture of which comprises one or more compounds of formula (I) in which Z¹ and Z², independently of one another, are a single bond, -CH₂CH₂-, -COO-, -OCO- or -C≡C-, (a) and (b), independently of one another, are trans-1,4-cyclohexylene, 1,4-phenylene, 2-fluoro-1,4-phenylene, 3-fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene or 3,5-difluoro-1,4-phenylene and one of (a) and (b) may also be pyrimidine-2,5-diyl, pyridine-2,5-diyl or trans-1,3-dioxane-2,5-diyl, X¹ and X², independently from one another, are H or F, Q is -CF₂-, -OCF₂-, -C₂F₄-, -OC₂F₄ or a single bond, Y is -H, -F, -Cl or -CN, n is 0, 1 or 2 and R is alkyl having up to 13 C atoms, in which one or two non-adjacent CH₂ groups can also be replaced by -O- and/or -CH=CH- and additionally one or more reactive liquid crystalline compounds preferably containing terminal ene-group.</p>		

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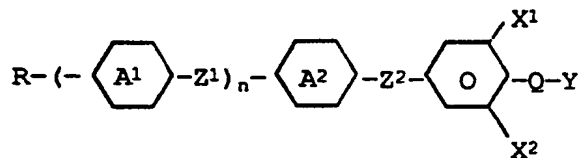
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ELECTROOPTICAL LIQUID CRYSTAL SYSTEM

The invention relates to an electrooptical liquid system

- 5 - which between 2 electrode layers contains a PDLC film comprising a liquid crystal mixture forming microdroplets in an optically isotropic, transparent polymer matrix,
- 10 - in which one of the refractive indices of the liquid crystal mixture is matched to the refractive index of the polymer matrix,
- 15 - which exhibits an electrically switchable transparency which is essentially independent of the polarization of the incident light,
- 20 - the precursor of the PDLC film of which comprises one or more monomers, oligomers and/or prepolymers and a photo-initiator, and is cured photoradically, and
- 25 - the liquid crystal mixture of which comprises one or more compounds of the formula I

25



I

in which

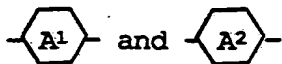
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
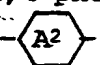
- 2 -

Z¹ and Z²

independently of one another, are a single bond, -CH₂CH₂-, -COO-, -OCO- or -C=C-,

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independently of one another, are trans-1,4-cyclohexylene, 1,4-phenylene, 2-fluoro-1,4-phenylene, 3-fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene or 3,5-difluoro-1,4-phenylene and one of  and  may also be pyrimidine-2,5-diyl, pyridine-2,5-diyl or trans-1,3-dioxane-2,5-diyl,

10

15

X¹ and X²

independently from one another, are H or F,

Q

is CF₂, OCF₂, C₂F₄, OC₂F₄ or a single bond,

20

Y

is H, F, Cl or CN,

n

is 0, 1 or 2, and

25

R

is alkyl having up to 13 C atoms, in which one or two non-adjacent CH₂ groups can also be replaced by -O- and/or -CH=CH-.

30

The preparation of PDLC (= polymer dispersed liquid crystal) films is described, for example, in US 4,688,900, Mol. Cryst. Liq. Cryst. Nonlin. Optic, 157, 1988, 427-441, WO 89/06264 and EP 0,272,585. In the so-called PIPS technology (= polymerization-induced phase separation) the liquid crystal mixture is first homogenously mixed with monomers and/or oligomers of the matrix-forming material; phase-separation is then induced by polymerization. Differentiation must further be made between TIPS (temperature-induced phase separation) and SIPS (solvent-induced phase separation) (Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt. 157 (1988) 427) both being also methods to produce PDLC films.

The process of preparation must be controlled very carefully in order to obtain systems with good electrooptical properties. F.G. Yamagishi et al., SPIE Vol. 1080, Liquid Crystal Chemistry, Physics and Applications, 1989, p.24 differentiate between a "Swiss cheese" and a "polymer ball" morphology. In the latter one, the polymer matrix consists of small polymer particles or "balls" being connected or merging into each other while in the Swiss cheese system, the polymer matrix is continuous and exhibits well defined, more or less spherical voids containing the liquid crystal. The Swiss cheese morphology is preferred because it exhibits a reversible electrooptical characteristic line while the polymer ball system shows a distinct hysteresis generally leading to a drastic deterioration of the electrooptical characteristic line when comparing the virgin and the second run.

According to Yamagishi et al., loc. cit., the Swiss cheese morphology is promoted in case the polymerization reaction runs via a step mechanism, and in WO 89/06264 it is pointed out that the step mechanism is favoured in case the precursor
5 of the polymer matrix consists of multifunctional acrylates and multifunctional mercaptanes.

In PDLC films, one of the refractive indices of the liquid crystal mixture, customarily the ordinary refractive index n_o ,
10 is selected in such a way that it more or less coincides with the refractive index n_p of the polymeric matrix. If no voltage is applied to the electrodes, the liquid crystal molecules in the droplets exhibit a distorted alignment, and incident light is scattered at the phase boundary between the poly-
15 meric and liquid crystal phases.

On applying a voltage, the liquid crystal molecules are aligned parallel to the field and perpendicular to the E vector of the transmitted light. Normally incident light
20 (viewing angle $\theta = 0^\circ$) now sees an optically isotropic medium and appears transparent.

No polarisers are required for operating PDLC systems, as a result of which these systems have high transmission. PDLC
25 systems provided with active matrix addressing have been proposed on the basis of these favourable transmission properties in particular for projection applications, but in addition also for displays having high information content and for further applications.
30

The liquid crystal mixtures used for producing PDLC systems have to meet a wide range of demands. One of the refractive indices of the liquid crystal mixture is selected such that it matches with the refractive index of the polymer matrix.

5 The term matching of refractive indices used here covers not only the case n_o (resp. another refractive index of the liquid crystal mixture) $\sim n_p$, but also the condition n_o (resp. another refractive index of the liquid crystal mixture) $< n_p$ which is sometimes chosen to reduce off-axis haze and enlarge

10 the view angle as is described, for example, in EP 0,409,442.

The liquid crystal mixture preferably has a positive dielectric anisotropy but the use of dielectrically negative liquid crystal mixtures (see, for example, WO 91/01511) or

15 two-frequency liquid crystal mixtures (see, for example, N.A. Vaz et al., J. Appl. Phys. 65, 1989, 5043) is also discussed.

Furthermore, the liquid crystal mixture should have a high clearing point, a broad nematic range, no smectic phases down

20 to low temperatures and a high stability and should be distinguished by an optical anisotropy Δn and a flow viscosity η which can be optimized with respect to the particular application, and by a high electrical anisotropy.

25 A series of matrix materials and polymerization processes have hitherto been proposed for producing PDLC systems. The PIPS, SIPS and TIPS technologies are described in some detail in Mol. Cryst. Liq. Cryst. Inc. Nonlin. Optics, 157, 1988, 427. The PDLC systems described in Mol. Cryst. Liq. Cryst.

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Inc. Nonlin. Optics, 157, 1988, 427 are based on an epoxy film, while in EP 0,272,585 acrylate systems are given. The PDLC system of WO 89/06264 is based on multifunctional acrylates and multifunctional thioles, and Y. Hirai et al., SPIE Vol. 1257, Liquid Crystal Displays and Applications, 1990, p.2 describe PDLC systems the precursor of the polymer matrix of which being based on monomers and oligomers. Further suitable matrix materials are described, for example, in US 3,935,337, WO 91/13126 and in further references.

Electrooptical systems containing PDLC films can be addressed passively or actively. Active driving schemes employing an active matrix having nonlinear addressing elements like, for example, TFT transistors integrated with the image point, are especially useful for displays with high information content.

When the PDLC system is addressed by means of an active matrix, a further far reaching criterion is added to the requirements listed so far which must be fulfilled by the cured polymer and the liquid crystal mixture being embedded in microdroplets. This is related to the fact that each image point represents a capacitive load with respect to the particular active nonlinear element, which is charged at the rhythm of the addressing cycle. In this cycle, it is of paramount importance that the voltage applied to an addressed image point drops only slightly until the image point is again charged in the next addressing cycle. A quantitative measure of the drop in voltage applied to an image point is the so-called holding ratio (HR) which is defined as the

ratio of the drop in voltage across an image point in the nonaddressed state and the voltage applied; a process for determining the HR is given, for example, in Rieger, B. et al., Conference Proceeding der Freiburger Arbeitstagung Flüssigkristalle (Freiburg Symposium on Liquid Crystals),
5 Freiburg 1989. Electrooptical systems having a low or relatively low HR show insufficient contrast.

A further serious problem is often that the liquid crystal
10 mixture has insufficient miscibility with the monomers, oligomers and/or prepolymers of the polymer used for forming the matrix, which limits in particular the use of PIPS technology in microdroplet matrix systems.

A further disadvantage is in particular that the liquid
15 crystal mixture or individual components of the liquid crystal mixture are in many cases distinguished by an excessively high and/or significantly temperature dependent solubility in the cured, matrix-forming polymer. If, for example, the
20 solubility or the temperature-dependence of the solubility of one or several components differs quite significantly from that of the remaining components, it may happen that the physical properties of the mixture and in particular also of the refractive indices n_e and n_o are substantially affected,
25 which disturbs the adjustment of n_o or n_e or another refractive index of the liquid crystal mixture to n_M , thus resulting in a deterioration of the optical properties of the system.

The "bleeding" described in EP 0,357,234, according to which at least some of the liquid crystal droplets have the tendency, when the matrix film is subjected to mechanical stress, to dissolve with diffusion of the liquid crystal to the film surface or into the matrix, is favoured by a high solubility of the liquid crystal mixture in the cured polymer.

Very important electrooptical parameters of electrooptical systems according to the preamble of claim 1 are the switching voltages and switching times. The threshold voltage V_{th} is usually defined as the voltage $V_{10,0,20}$ at which a transmission of 10 % is observed at a temperature of 20 °C and under a viewing angle Θ of 0° while the saturation voltage is the lowest voltage for which the maximum transmission is observed at 20 °C and a viewing angle of 0°. The switching on time t_{on} is usually reported as the time necessary for the transmission to rise from 0 % to 90 % of the maximum transmission when the saturation voltage is applied while t_{off} is the time necessary for the transmission to drop from 100 % to 10 % when the voltage is switched off.

In US 4,673,255 it is shown that a correlation exists between the mean size of the microdroplets on the one hand and the switching voltages and switching times of the system on the other hand. Generally, relatively small microdroplets cause relatively high switching voltages, but relatively short switching times and vice versa.

Experimental methods for influencing the average droplet size are described, for example, in US 4,673,255 and in J.L. West, Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt., 157, 1988, 427. In US 4,673,255, average drop diameters between 0.1 μm and 8 μm are given, while, for example, a matrix which is based on a glass monolith has pores having a diameter between 15 and 2,000 Å. For the mesh width of the network of PN systems, a preferred range between 0.5 and 2 μm is given in EP 0,313,053.

The switching voltage, however, must not be chosen too high because of several reasons (power consumption, safety of operation, compatibility with conventional modules of microeletronic).

On the other hand, high switching times are generally not tolerable which is evident in case of display applications, but which is also true for many other applications. Low switching time are also often required at lower temperature because the systems according to the preamble are also discussed for out-door applications.

It is true that considerable efforts have already been undertaken hitherto in order to optimize PDLC systems with respect to the liquid crystal mixture used and the polymer system. On the other hand, however, it is still an open problem how to realize PDLC films which are characterized both by low switching times especially at low temperatures and at the same time by advantageous values of the switching voltages.

No method is known so far by which switching voltages and switching times can be adjusted with respect to the intended application more or less independently from each other.

Furthermore, only few investigations of PDLC systems having active matrix addressing can be found in the literature, and no concepts have so far been proposed for providing electrooptical systems having

5

- a high HR and a low temperature dependence of HR
- advantageous values of the switching voltages, and
- 10 - low switching times, especially at low temperatures.

Consequently, there is a high demand for PDLC systems which fulfill to a large extent the requirements described and which exhibit advantageous values of the switching voltages, and, in particular, low switching times especially at low
15 temperatures. Furthermore, there is a high demand for actively addressed PDLC systems which exhibit a high HR and a low temperature dependence of HR in addition to low switching times.

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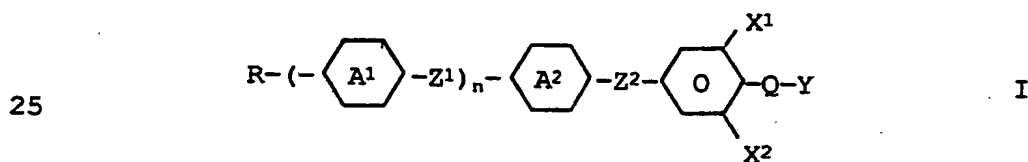
The object of the invention was to provide PDLC systems of this type and precursors of these PDLC systems containing monomers, oligomers and/or prepolymers of the polymer used and a liquid crystal mixture. Other aims of the present
25 invention are immediately evident to the person skilled in the art from the following detailed description.

It has been found that PDLC systems which are characterized by low switching times can be obtained if one or more reactive liquid crystalline compounds are added to its liquid
30 crystal mixture.

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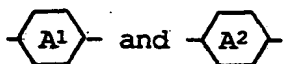
The invention thus relates to an electrooptical liquid crystal system



- which between 2 electrode layers contains a PDLC film comprising a liquid crystal mixture forming microdroplets in an optically isotropic, transparent polymer matrix,
- in which one of the refractive indices of the liquid crystal mixture is matched to the refractive index of the polymer matrix,
- which exhibits an electrically switchable transparency which is essentially independent of the polarization of the incident light,
- the precursor of the PDLC film of which comprises one or more monomers, oligomers and/or prepolymers and a photoinitiator, and is cured photoradically, and
- the liquid crystal mixture of which comprises one or more compounds of the formula I



in which

- 30 Z^1 and Z^2 independently of one another, are a single bond, $-\text{CH}_2\text{CH}_2-$, $-\text{COO}-$, $-\text{OCO}-$ or $-\text{C}=\text{C}-$,



independently of one another, are trans-1,4-cyclohexylene, 1,4-phenylene, 2-fluoro-1,4-phenylene, 3-fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene or 3,5-difluoro-1,4-phenylene and one of  and  may also be pyrimidine-2,5-diyl, pyridine-2,5-diyl or trans-1,3-dioxane-2,5-diyl,

10

X¹ and X²

independently from one another, are H or F,

15

Q

is CF₂, OCF₂, C₂F₄ or a single bond,

Y

is H, F, Cl or CN,

n

is 0, 1 or 2, and

20

R

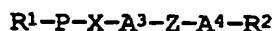
is alkyl having up to 13 C atoms, in which one or two non-adjacent CH₂ groups can also be replaced by -O- and/or -CH=CH-,

25

characterized in that the liquid crystal mixture additionally contains one or more reactive liquid crystalline compounds in order to obtain improved switching times especially at low temperatures. Part of the reactive liquid crystalline compounds which can be used in the electrooptical systems according to the present invention is new, and such new reactive liquid crystalline compounds are also claimed.

30

Specifically, the present invention also relates to reactive liquid crystalline compounds of formula III



III

5

wherein

O

10 R^1 is $CH_2 = CW-COO-$, $CH_2 = CH-$, $HW-C-C-$, $HWN-$, $HS-CH_2-(CH_2)_m-$
 $COO-$ with W being H, Cl or alkyl with 1-5 C atoms and m
 being 1-7,

15 P is alkylene with up to 12 C atoms, it being also possible
 for one or more CH_2 groups to be replaced by O,

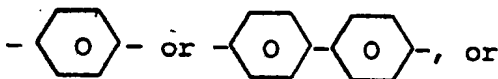
X is $-O-$, $-S-$, $-COO-$, $-OCO-$ or a single bond,

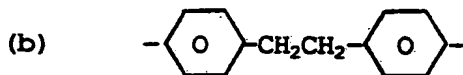
20 R^2 is alkyl radical with up to 15 C atoms which is unsubsti-
 tuted, mono-or polysubstituted by halogen, it being also
 possible for one or more CH_2 groups in these radicals to
 be replaced, in each case independently of one another,
 by $-O-$, $-S-$, $-CO-$, $-OCO-$, $-CO-O-$ or $-O-CO-O-$ in such a
 manner that oxygen atoms are not linked directly to one
 another, $-CN$, $-F$, $-Cl$, or alternatively R^2 has one of the
 25 meanings given for R^1-P-X ,

A^3 is a 1,4-phenylene or a naphthalene-2,6-diyl radical which
 is unsubstituted or substituted with 1 to 4 halogen
 atoms,

30

A^4 is (a)





it being possible for radicals (a) and (b) to be substituted by CN or halogen and one of the 1,4-phenylene groups in (a) and (b) can also be replaced by a 1,4-phenylene radical in which one or two CH groups are replaced by N, and

Z is -CO-O-, -O-CO-, -CH₂CH₂- or a single bond.

The construction of the electrooptical system according to the present invention corresponds to the customary mode of construction for systems of this type. The term customary mode of construction is in this case broadly interpreted and includes all adaptations and modifications.

Thus, for example, the matrix formed by the transparent medium in which the liquid crystal mixture is microdispersed or microencapsulated, is arranged between conducting electrodes like a sandwich.

The electrodes are applied, inter alia, to substrate sheets of, for example, glass, plastic or the like; if desired, however, the matrix can also be provided directly with electrodes so that the use of substrates can be avoided. One of the electrodes forms an active matrix while the other one acts as counter electrode.

The precursor of the PDLC film comprising the precursor of the matrix, the liquid crystal mixture and one or more reactive liquid crystalline compounds can be capillary filled between two substrates which are provided with electrode layers, and the precursor of the PDLC film is subsequently cured, for example, by irradiation with UV light. Another technique comprises coating of the precursor of the PDLC film on a substrate with subsequent curing. The film may be peeled off and arranged between 2 substrates provided with electrode layers. It is also possible that the substrate onto which the precursor of the PDLC film is applied exhibits an electrode layer so that the electrooptical system can be obtained by applying a second electrode layer and, optionally, a second substrate onto the coated and cured film.

The electrooptical system according to the invention can be operated reflectively or transmissively so that at least one electrode and, if present, the associated substrate are transparent. Both systems customarily contain no polarizers, as a result of which a distinctly higher light transmission results. Furthermore, no orientation layers are necessary, which is a considerable technological simplification in the production of these systems compared with conventional liquid crystal systems such as, for example, TN or STN cells.

Processes for the production of PDLC films are described, for example, in US 4,688,900, US 4,673,255, US 4,671,618, WO 85/0426, US 4,435,047, EP 0,272,595, Mol. Cryst. Liq. Cryst, Inc. Nonlin. Opt. 157 (1988) 427, Liquid Crystals, 3

(1988) 1543, EP 0,165,063, EP 0,345,029, EP 0,357,234 and EP 0,205,261. The formation of the PDLc film is generally achieved by 3 basic methods: in the PIPS technique (= PIPS, polymerization induced phase separation) the liquid crystal mixture, and optionally further additives, are dissolved in the precursor of the matrix material, and subsequently polymerization is started. TIPS (= thermally induced phase separation) means that the liquid crystal mixture is dissolved in the melt of the polymer followed by cooling while SIPS (= solvent induced phase separation) starts with dissolving the polymer and the liquid crystal mixture in a solvent with subsequent evaporation of the solvent. The invention is, however, not restricted to these specific techniques but covers also electrooptical systems obtained by modified methods or other methods. The use of the PIPS technology is usually preferred.

The thickness d of the electrooptical system is customarily chosen to be small in order to achieve a threshold voltage V_{th} which is as low as possible. Thus, for example, layer thicknesses of 0.8 and 1.6 mm are reported in US 4,435,047, while values for the layer thickness between 10 and 300 μm are given in US 4,688,900 and between 5 and 30 μm in EP 0,313,053. The electrooptical systems according to the invention only have layer thicknesses d greater than a few mm in exceptional cases; layer thicknesses below 200 μm and especially below 100 μm are preferred. In particular, the layer thickness is between 2 and 100 μm , especially between 3 and 50 μm and very particularly between 3 and 25 μm .

An essential difference between the electrooptical liquid crystal system according to the present invention and those customary hitherto, however, consists in that the liquid crystal mixture contains one or more reactive liquid crystalline compounds.

The term reactive liquid crystalline compounds denotes rod-like compounds of formula II

10 $R'-G'-R''$

II

wherein at least one of the terminal groups R' and R'' is a reactive group exhibiting one reaction site such as a hydroxyl group $HOW_2'C-$, a thiol group $HSW_2'C-$, an amino group $HW'N-$, a carboxyl group, an epoxid group $W'_2C-CW'-$ or an iso-

15 cyanate group $O=C-N-$, or a polymerizable reactive group exhibiting two or more reactive sites such as a vinyl type group $W_2'C=CW'-$, a (meth)acrylate type group $W_2'C=C-COO-$,
 20 $\begin{array}{c} | \\ (CH_3) \end{array}$

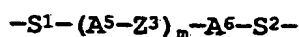
a styrene type group $-O-CW'=CW'_2$ with W' being independently from each other H or an alkyl group with 1-5 C atoms,

25 the other terminal group is also, independently from the first terminal group, a reactive group with one or more reactive sites or an alkyl radical with up to 15 C atoms which is unsubstituted or mono- or polysubstituted by halogene, it being also possible for one or more CH_2 groups in
 30 these radicals to be replaced, in each case independently of one another, by $-O-$, $-S-$, $-CO-$,

-OCO-, -CO-O- or -O-CO-O- in such a manner that O atoms are not linked directly to one another,

G is a rod-like diyl group of the formula

5



with S¹ and S² being independently from each other alkylene groups with 0-20 C atoms which can be linear or branched, it also being possible for one or more CH₂ groups to be replaced, in each case independently from each other, by -O-, -CO-, -S- or -NW'- with the proviso that O atoms are not linked directly to one another,

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A⁵ and A⁶ denote, independently from each other,

a) a cyclohexylene group, wherein one or two non-adjacent CH₂ groups may be replaced by O or S atoms,

20

b) an unsubstituted 1,4-phenylene group wherein one to three CH groups may be replaced by -N- or a 1,4-phenylene group which is mono- or polysubstituted by F, Cl and/or CH₃,

25

c) a bicyclo(2,2,2)octylene group, a naphthalene-2,6-diyl group, a decahydronaphthalene-2,6-diyl group or 1,2,3,4-tetrahydronaphthalene group,

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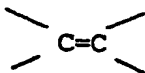
Z³ is independently from each other -CO-O-, -O-CO-, -CH₂CH₂-, -CH₂O-, -OCH₂-, -C≡C- or a single bond, and

m denotes 1, 2, 3, or 4.

Above and below, the term reactive liquid crystalline compounds refers to reactive rod-like molecules like, for example, those of formula III or other rod-like reactive compounds which may be enantiotropic, monotropic or isotropic, preferably, however, enantiotropic or monotropic.

In a preferred embodiment of the eletrooptical systems according to the present invention, at least one of R' and R'' preferably is or contains an ene-group

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When polymerizing the precursor of the PDLC film by impact of thermal energy or irradiation, usually in presence of an ionic or radical polymerization initiator, the reactive liquid crystalline compounds being contained in the liquid crystalline phase when phase separation starts, are reacting with each other thus obviously forming some internal structure in the liquid crystalline microdroplets. This structure may be considered as some kind of network which divides the liquid crystalline microdroplet in some smaller sub-compartments which may be in contact with each or be separated from each other. The term "some kind of network" is to be understood in a wide sense and comprises a wide range of geometries of the internal structure. The surrounding polymer matrix and the internal structure may be connected or not.

30

In another embodiment of the electrooptical systems according to the present invention, at least one of R' and R'' is a reactive group exhibiting one reactive site, and in particular a hydroxyl group, a thiol group, a carboxyl group, an amino group or an isocyanato group. Reactive liquid crystalline compounds of this type can be attached to the surrounding polymeric matrix in a coupling reaction or they can also react with each other, especially in case of suitably chosen co-reactive compounds of formula II. The coupling reaction may occur during the polymerization of the surrounding matrix or afterwards as a polymer-analogous reaction. In case of reactive liquid crystalline compounds of formula II exhibiting only one reactive group of the one reaction site type, it is assumed that the reactive group is coupled to the inner surface of the polymeric matrix with the rest of the molecule being arranged in the liquid crystalline microdroplet, inducing there same kind of internal structure.

The addition of one or more reactive liquid crystalline compounds of formula II exhibiting two reactive groups R' and R'' to the liquid crystalline mixture is generally preferred. Also preferred is the addition of a reactive liquid crystalline component, containing at least two different reactive liquid crystalline compounds according to formula II at least one of which contains 2 reactive groups R' and R''. Reactive liquid crystalline components containing at least one reactive liquid crystalline compound with one reactive group R' (monofunctional reactive liquid crystalline compound) and at least one reactive liquid crystalline compound with two

reactive compounds (difunctional reactive liquid crystalline compound) often are especially preferred while reactive liquid crystalline components consisting of one or more monofunctional reactive liquid crystalline compounds usually are less advantageous.

Especially preferred difunctional reactive liquid crystalline compounds are di-ene type compounds such as divinyls, diacrylates or dimethacrylates, furthermore diols, dithiols and diisocyanates, but also compounds with different reactive groups such as ene-ols, ene-thiols, vinylacrylates etc.

The groups S^1 and S^2 acting as spacer groups between the reactive groups R' and R'' and the mesogenic core $-(A^5-Z^3)_m-A^6$ are independently from each other an alkylene group with 0-20 C atoms which can be linear or branched, it also being possible for one or more CH_2 groups to be replaced, in each case independently from each other by $-O-$, $-CO-$, $-S-$ or $-NW'-$ with the proviso that oxygen atoms are not linked directly to one another.

The length and the structure of the groups S^1 and S^2 determine whether the mesogenic group exhibits a more or less pronounced degree of flexibility. The following list of suitable groups S^1 and S^2 is intended to be illustrative and not limiting:

ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxybutylene, ethylenethio-

ethylene, ethylene-N-methyliminoethylene, (1-oxy)methylene-
 oyloxy, (2-oxy)ethyleneoyloxy, (3-oxy)propyleneoyloxy, (4-
 oxy)butyleneoyloxy, (5-oxy)pentyleneoyloxy, (6-oxy)hexyl-
 eneoyloxy, (7-oxy)heptyleneoyloxy, (8-oxy)octyleneoyloxy,
 5 (1-oxy)methyleneoxycarbonyl (2-oxy)ethyleneoxycarbonyl,
 (3-oxy)propyleneoxycarbonyl, (4-oxy)butyleneoxycarbonyl,
 (5-oxy)pentyleneoxycarbonyl, (6-oxy)hexyleneoxycarbonyl,
 (7-oxy)heptyleneoxycarbonyl and (8-oxy)octyleneoxycarbonyl.

10 The mesogenic core $-(A^5-Z^3)_m-A^6$ of the reactive liquid crys-
 talline compounds can exhibit 2, 3, 4 or 5 rings:

- | | | |
|----|---|-----|
| | $-A^5-Z^3-A^6-$ | (1) |
| | $-A^5-Z^3-A^5-Z^3-A^6-$ | (2) |
| 15 | $-A^5-Z^3-A^5-Z^3-A^5-Z^3-A^6-$ | (3) |
| | $-A^5-Z^3-A^5-Z^3-A^5-Z^3-A^5-Z^3-A^6-$ | (4) |

Especially preferred for use in the electrooptical systems
 according to the present invention are reactive liquid crys-
 20 talline compounds exhibiting 2-, 3- or 4-ring mesogenic
 groups according to formula (1)-(3) and in particular 2- or
 3-ring mesogenic groups according to formula (1) or (2).

In the following, for sake of simplicity, Cyc is a 1,4-cyclo-
 25 hexylene group, Phe is a 1,4-phenylene group which can be
 unsubstituted or mono-, di- or trifluorinated, Dio is a
 1,3-dioxane-2,5-diyl group, Pyd is a pyridine-2,5-diyl group,
 Pyr is a pyrimidine-2,5-diyl group, Pip is a piperidine-1,4-
 diyl group, Bio is a 1,4-bicyclo(2,2,2)octylene group, Nap is
 30

a naphthalene-2,6-diyl group and Thn is a 1,2,3,4-tetrahydronaphthalene-2,6-diyl group; the abbreviations Dio, Pyd, Pyr and Pip comprise all possible positional isomers.

- 5 Especially preferred is the following smaller group of mesogenic cores according to formula (2):

	-Phe-Z ³ -Phe-	(2) a
	-Cyc-Z ³ -Cyc-	(2) b
10	-Phe-Z ³ -Cyc-	(2) c
	-Pyr-Z ³ -Phe-	(2) d
	-Pyd-Z ³ -Phe-	(2) e
	-Dio-Z ³ -Cyc-	(2) f

- 15 In the structures according to formulae (2) a-(2) f Z³ preferably is -COO-, -OCO-, -CH₂CH₂- or a single bond. Electrooptical systems according to the present invention containing one or more reactive liquid crystalline compounds containing a two-ring mesogenic structure according to formulae (2) a-(2) c
- 20 generally exhibit especially advantageous properties.

- Especially preferred is also the use of reactive liquid crystalline compounds according to formulae II which contain a mesogenic group with 3 rings according to formulae
- 25 (3) a-(3) f:

	-Phe-Z ³ -Phe-Z ³ -Phe-	(3) a
	-Cyc-Z ³ -Phe-Z ³ -Phe-	(3) b
30	-Cyc-Z ³ -Cyc-Z ³ -Phe-	(3) c

-Cyc-Z ³ -Cyc-Z ³ -Cyc-	(3) d
-Pyr-Z ³ -Phe-Z ³ -Phe-	(3) e
-Pyd-Z ³ -Phe-Z ³ -Phe-	(3) f

5 Electrooptical systems containing both at least one 2-ring reactive liquid crystalline compound with a mesogenic group according to formula 2(a)-2(f) and at least one 3-ring reactive liquid crystalline compound with a mesogenic group according to formulae 3(a)-3(f) are preferred.

10

In the mesogenic structures of formulae (3)a-(3)f Z³ preferably is independently from each other a single bond, -COO-, -OCO- or -CH₂CH₂-. Especially preferred are the following combinations with — representing a single bond:

15

first linking group	second linking group
—	—
—	CH ₂ CH ₂
CH ₂ CH ₂	CH ₂ CH ₂
OCO	COO

20

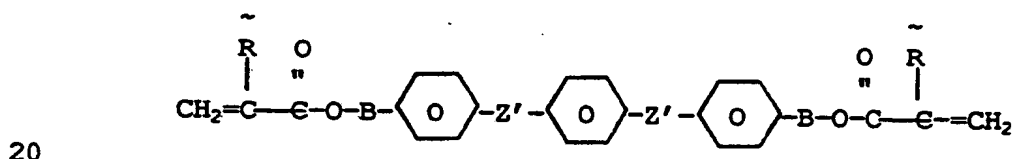
25 Electrooptical systems containing one or more reactive liquid crystalline compounds according to formula II which contain a mesogenic group with 4 rings according to formulae (4)a-(4)f exhibit advantageous properties:

30

- Cyc-Z³-Phe-Z³-Phe-Z³-Phe- (4) a
 -Cyc-Z³-Cyc-Z³-Phe-Z³-Phe- (4) b
 -Cyc-Z³-Cyc-Z³-Cyc-Z³-Phe- (4) c
 -Cyc-Z³-Phe-Z³-Phe-Z³-Cyc- (4) d
 5 -Phe-Z³-Phe-Z³-Phe-Z³-Phe- (4) e
 -Cyc-Z³-Cyc-Z³-Cyc-Z³-Cyc- (4) f

In the structures according to formula (4) a-(4) f at least one
 of Z³ preferably is a single bond. The other two linking
 10 groups preferably denote independently from each other a
 single bond, -COO-, -OCO- OR -CH₂CH₂-.

Reactive liquid crystalline compounds have hitherto been
 known. EP 0,261,712, for example, describes liquid crystal-
 15 line diacrylates of the formula



wherein R is a hydrogen atom or a methyl group, Z' is inde-
 pendently from each other -COO- or -OCO- (≡ -OOC), and B is a
 flexible spacer, chosen from the group consisting of -(CH₂)_x-,
 25 -(CH₂)_x-O-, -(Si(CH₃)₂-O)_x- wherein x = 1-5 or -(CH₂-CH₂-O)_y-O
 wherein y = 1-8, for use in orientation layers of LCDs.

Hikmet describes in Mol. Cryst. Liq. Cryst., 198, 357-70
 anisotropic gels which were obtained by curing a mixture of a
 30 low-molecular weight liquid crystal and liquid crystalline
 diacrylates.

The use of reactive liquid crystalline compounds in PDLC systems, however, is not reported in literature and it was completely surprising that PDLC systems the liquid crystalline mixture of which additionally contains one or more
5 reactive liquid crystalline compounds, exhibits short switching times even at low temperature and simultaneously advantageous values of the switching voltages.

In the following table 1, the electrooptical properties of
10 systems according to the invention are compared with the properties of a conventional PDLC system (comparative example 1) resp. with the properties of PDLC systems containing non liquid-crystalline reactive monomers. NOA 65 (prepared by Norland Products) is used as the precursor of the matrix, and
15 E7 from Merck Ltd., GB, which consists of

51.0 %	of 4-pentyl-4'-cyanobiphenyl
25.0 %	of 4-heptyl-4'-cyanobiphenyl
16.0 %	of 4-octoxy-4'-cyanobiphenyl
20 8.0 %	of 4-pentyl-4''-cyanoterphenyl

is used as liquid crystalline mixture. The additives used in the respective experiments, and their amount with respect to the mass of the precursor of the PDLC film are given in table
25 1. The systems in each case are prepared by mixing and optionally heating the constituents of the precursor of the PDLC film to form a clear solution which subsequently is capillary filled together with spacers between 2 glass substrates which are provided with electrode layers. The system
30 is then irradiated with light of suitable wavelength in order to cure the precursor; NOA 65 the composition of which is

given in Molecular Crystals Liquid Crystals, 196 (1991),
89-102, contains benzophenone as a photoinitiator. The
response time τ given in table 1 which is the sum of switching
on and switching off times, is measured at a drive voltage of
5 $1.5 \times V_{sat}$ with V_{sat} being the lowest voltage for which maximum
transmission is observed.

It is evident from table 1 that the addition of non-liquid
crystalline reactive compounds to the precursor of the PDLC
10 film does not affect the electrooptical properties of the
cured PDLC film very much (comparative experiments no. 2 and
no. 3). Both the saturation voltage and the switching times
are comparable to the values obtained for a conventional
system without any reactive additives (comparative experiment
15 no. 1). The reason most presumably is that the non-liquid
crystalline reactive additives are incorporated into the
polymer matrix and do not give rise to an internal structure
of the liquid crystalline microdroplets.

20 Contrary to this, experiments no. 1-4 show that a drastical
reduction of switching times is obtained in case a reactive
liquid crystalline compound is added to the precursor of the
PDLC film. Especially pronounced is the reduction of switch-
ing time at the lower temperature of 0 °C. While the conven-
25 tional PDLC system of comparative experiment no. 1 exhibits a
switching time τ (0 °C) = 283 ms, the switching times of the
systems according to the invention as prepared in experiments
no. 2-4 exhibit switching times at 0 °C between 10 and 47 ms.

- 28 a -

Table 1/part one

Composition of the precursor of the PDLC film

Experiments	Percentage of NOA 65	Percentage of E 7
Comparative experiment No. 1	40 %	60 %
Comparative experiment No. 2	40 %	58 %
Comparative experiment No. 3	40 %	58 %
Experiment No. 1	40 %	58 %
Experiment No. 2	40 %	58 %
Experiment No. 3	40 %	59,5 %
Experiment No. 4	40 %	59,9 %

Table 1/part two

Composition of the precursor of the PDLC film

Experiments	Reactive additive
Comparative experiment No. 1	-
Comparative experiment No. 2	bisphenol A diacrylate
Comparative experiment No. 3	$\text{CH}_2=\text{CHCOO}-\text{C}_6\text{H}_3(\text{F})(\text{Cl})$
Experiment No. 1	$\text{CH}_2=\text{CHCO}_2(\text{CH}_2)_6\text{O}-\text{C}_6\text{H}_4-\text{COOC}_2\text{H}_4\text{OOC}-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_6\text{OOCCH}=\text{CH}_2$
Experiment No. 2	$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_6\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{OOC}-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_6\text{OOCCH}=\text{CH}_2$
Experiment No. 3	$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_6\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{OOC}-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_6\text{OOCCH}=\text{CH}_2$
Experiment No. 4	$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_6\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{OOC}-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_6\text{OOCCH}=\text{CH}_2$

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Table 1/part three

Composition of the precursor of the PDLC film		Electrooptical properties		
Experiments	Percentage reactive	τ (20 ° C)/ms	τ (0 ° C)/ms	V_{sat}/V
Comparative experiment No. 1	-	33	283	19
Comparative experiment No. 2	2 %	48	193	24
Comparative experiment No. 3	2 %	41	326	17
Experiment No. 1	2 %	10	30	70
Experiment No. 2	2 %	3	10	80
Experiment No. 3	0.5 %	16	28	43
Experiment No. 4	0.1 %	31	47	28

When comparing experiments no. 2-4 it can be concluded that the addition of a diacrylate component has contrary effects with respect to switching times and switching voltages. If the concentration of the diacrylate compound

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is chosen to be 2 % with respect to the mass of the precursor of the PDLC film, the switching times both at 20 °C and 0 °C are very low while the saturation voltage is relatively high and distinctly higher than the saturation voltage of the conventional system according to comparative experiment no. 1.

10

Reducing the concentration of the diacrylate compound as low as 0.1 % gives a saturation voltage of 28 V which is comparable to the saturation voltage of the conventional system according to comparative experiment no. 1, but a distinctly lower switching time especially at 0 °C. The conditions of preparation are the same in all experiments listed in table 1 (mixing temperature of the precursor of the PDLC matrix, cooling rate, etc.) so that the distribution of microdroplet diameters can be assumed to be more or less the same.

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Table 2 summarizes the electrooptical properties of systems each of them containing only one monofunctional reactive liquid crystalline compound. It can be taken from table 2 that the addition of monofunctional reactive liquid crystalline compounds alone is often less advantageous. Both in experiment no. 5 and no. 6 the switching times at least of

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0 °C are inferior to the switching times of the conventional PDLC system according to comparative experiment No. 1. Especially disadvantageous is often the addition of monofunctional reactive liquid crystalline compounds wherein the non-reactive terminal group is a nitrile group. The use of monofunctional reactive liquid crystalline compounds with a less polar or unpolar non-reactive terminal group such as F, Cl, CF₃, OCF₃, OCHF₂, alkyl or alkoxy, however, and/or the use of reactive liquid crystalline components containing at least one difunctional and at least one monofunctional liquid crystalline compound, is often preferred.

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Table 2/part one

Composition of the precursor of the PDLC film

Experiments	Percentage of NOA 65	Percentage of E 7
Experiment No. 5	40 %	58 %
Experiment No. 6	40 %	58 %

Table 2/part two

Composition of the precursor of the PDLC film

Experiments	Reactive additive
Experiment No. 5	$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_7\text{COO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_3(\text{F})\text{OC}_8\text{H}_{17}$
Experiment No. 6	$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_7\text{COO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4\text{CN}$

Table 2/part threeComposition of the
precursor of the PDLC film

Electrooptical properties

Experiments	Percentage reactive	τ (20 ° C)/ms	τ (0 ° C)/ms	V_{sat}/V
Experiment No. 5	2 %	31	>500	50
Experiment No. 6	2 %	500	-	13

Based on the experiments summarized in table 1 and 2 as well as on further extensive experimental studies, the present inventors have developed the following ideas in order to explain the effects observed when adding reactive liquid crystalline compounds to the precursor of the PDLC film:

The reactive liquid crystalline compounds which are completely soluble (i.e. soluble at any concentration ratio of liquid crystal mixture and reactive additive) or at least highly soluble in the liquid crystal mixture, are polymerized and form a network or some other kind of structure within the droplets. The switching times are the lower the more close-meshed the substructure is. The reactive liquid crystalline compound binds into the interface of polymeric matrix and liquid crystal micro-droplet which results in increased anchoring and hence restoring forces on the components of the liquid crystal mixture. This leads to an increase of the switching voltages which is the more pronounced the higher the concentration of the reactive liquid crystalline compounds is. The concentration of the reactive liquid crystalline component has therefore to be adjusted properly in order to realize a drastical reduction of switching times in connection with no or only a tolerable increase in switching voltages.

The explanation outlined is to be understood as hypothesis which does not restrict the present invention.

In extensive experiments it was found out that the concentration of the reactive liquid crystalline component which consists of one or more reactive liquid crystalline compounds, must not be chosen too high and preferably is not more than 5 % and especially less than 2.5 % with respect to the mass of the precursor of the PDLC film. Particularly preferred are electrooptical systems according to the present invention the reactive liquid crystalline component of which amounts to not more than 1 %.

10

The reactive liquid crystalline compounds can be chosen from the great pool of known and new reactive liquid crystalline compounds embraced by formula II. The reactive liquid crystalline compounds preferably exhibit a high or very high solubility in the liquid crystal mixture.

15

The reactive liquid crystalline component preferably contains not more than 10 and in particular not more than 5 reactive crystalline compounds. Difunctional reactive liquid crystalline compounds are generally preferred and in case of these compounds, the reactive liquid crystalline component preferably contains 1-6, especially 1-3 and in particular not more than 2 reactive liquid crystalline compounds. Further preferred are reactive liquid crystalline components comprising at least one difunctional and one monofunctional reactive liquid crystalline compound. Further preferred are reactive liquid crystalline components comprising at least one monofunctional reactive liquid crystalline compound with the second terminal group being F, Cl, CF₃, OCF₃, OCHF₂ or non-polar group such as alkyl or alkoxy.

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The present inventors further observed that electrooptical systems according to the present invention are characterized by advantageous electrooptical properties and that they exhibits, in particular, no or only very little memory effect.

This memory effect which is often observed with conventional electrooptical systems the liquid crystal mixture of which contains no reactive liquid crystalline compounds, can be seen in Fig. 1-3 giving electrooptical characteristic lines for a conventional system the precursor of which has the following composition:

15	Liquid crystal mixture	60	% of BL036
	Precursor of the matrix	3.96 %	of TMPTMP
		18.0 %	of EHA
		4.8 %	of HDDA
		12.24 %	of E 270
20		1.0 %	of D 1173 (photo-initiator)

BL036 is a liquid crystal mixture available through ML, Poole, GB; TMPTMP is trimethylolpropanetri(3-mercaptopropionate); EHA is 2-ethyl-hexanolacrylate; HDDA is hexanedioldiacrylate, E 270 is a commercially available oligomer (Ebecryl 270, aliphatic urethane diacrylate, molecular weight $\approx 1,200$) and D 1173 is Darocur 1173 available through E. Merck, Darmstadt.

Fig. 1 shows the electrooptical characteristic line for this system at 20 °C ($d = 20 \mu\text{m}$); it exhibits an excellent electrooptical behaviour and no memory effect: when switched on and off, the system has the same off-state transmission (or better opacity) as in the initial unswitched state.

The situation changes for higher temperatures. This can be seen from Fig. 2 which shows an electrooptical curve and the off-state transmission for the same system at 70 °C. When switched off, the transmission is not as low as in the initial, unswitched state. This effect which is observed for most conventional systems especially at higher temperature is termed as memory effect.

Fig. 3 shows electrooptical curves for this system at 70 °C which were recorded after the off-switching in Fig. 2. When re-switched, the transmission starts at the high level of Fig. 2 and stops at this level during subsequent operations.

The system can be fully recovered only when it is being cooled to lower temperatures of, for example, 20 °C but the effect appears again when returning to higher temperatures of operation.

This effect is especially disadvantageous if the electrooptical system is to be operated over a wide range of temperatures, like, for example, in the case of out-door displays, transportable computers etc.

The present inventors now found that the electrooptical systems according to the present invention are characterized by a drastically reduced memory effect as can be seen from Fig. 4 showing an electrooptical characteristic line for a system according to the present invention the precursor of which contains 59.8 % of BL036, 0.2 % of



and the same precursor of the matrix used for the conventional systems of Fig. 1-3; $d = 20 \mu\text{m}$. Fig 5 shows the electrooptical characteristic line for this system according to the present invention at 20°C , which is excellent and only shows a slight increase with respect to V_{sat} when compared to the system of Fig. 1. The properties of the systems of Fig. 1 and Fig. 5 are compared in the following table with T_{on} resp. T_{off} being on-state resp. off-state transmission.

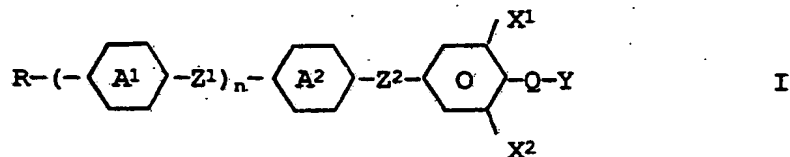
	V_{sat}	T_{on}	T_{off}
System of Fig. 1	23.6	0.185	0.004
System of Fig. 5	30.1	0.874	0.005

The memory effect can be completely suppressed if the concentration of the reactive liquid crystalline component is chosen to be higher, as can be seen from Fig. 6. This Fig. shows an electrooptical curve at 70°C for a system according to the present invention which contains 58 % of BL036, 2 % of the reactive liquid crystalline compound used in Fig. 4 and the same precursor of the matrix as in the system of Fig. 4.

No memory effect is observed but the saturation voltage is at the same time considerably increased in comparison to the saturation voltage of the system of Fig. 1 as was noted already above. Electrooptical systems according to the present invention the reactive liquid crystalline component of which amounts do not more than 1 % quite generally represent a very low memory effect on the one hand and a small and at any rate tolerable increase of the saturation voltage on the other hand.

Summarizing it can be stated that the electrooptical systems according to the present invention are characterized by advantageous electrooptical properties and, in particular, by low switching times, especially at low temperatures, and a considerably reduced memory effect.

The liquid crystalline mixture used in the electrooptical systems according to the invention contains at least 2 non-reactive liquid crystalline compounds which, for the sake of simplicity, are also simply termed as liquid crystalline compounds. The liquid crystalline mixture preferably comprises at least one compound of formula I

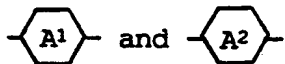




in which

Z¹ and Z²

independently of one another, are a single bond, -CH₂CH₂-, -COO-, -OCO- or -C=C-,

5



independently of one another, are trans-1,4-cyclohexylene, 1,4-phenylene, 2-fluoro-1,4-phenylene, 3-fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene or 3,5-difluoro-1,4-phenylene and one of  and  may also be pyrimidine-2,5-diyl, pyridine-2,5-diyl or trans-1,3-dioxane-2,5-diyl,

10

15

X¹ and X²

independently from one another, are H or F,

Q

is CF₂, OCF₂, C₂F₄ or a single bond,

20

Y

is H, F, Cl or CN,

n

is 0, 1 or 2, and

25

R

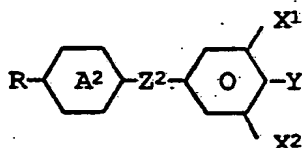
is alkyl having up to 13 C atoms, in which one or two non-adjacent CH₂ groups can also be replaced by -O- and/or -CH=CH-.

30

In the following, for the sake of simplicity, Phe is 1,4-phenylene, Phe.2F is 2-fluoro-1,4-phenylene, Phe.3F is 3-fluoro-1,4-phenylene, Cyc is trans-1,4-cyclohexylene, Pyr is pyrimidine-2,5-diyl and Pyd is pyridine-2,5-diyl, the two
 5 abbreviations Pyr and Pyd comprising in each case the two possible positional isomers. Furthermore, Phe.(F) is intended to designate a 1,4-phenylene group which may be unsubstituted or monosubstituted by fluorine in the 2 or 3 position.

Phe.2F3F and Phe.3F5F are a 1,4-phenylene group which is
 10 difluorinated in the 2 and 3, and 3 and 5 position respectively. Liquid crystal compounds according to formula I, wherein Y is H, F or Cl will be termed in the following as SFM compounds (superfluorinated materials) according to formula I.

15 Electrooptical systems whose liquid crystal mixture contains one or more binuclear compounds of the formula I2 are preferred:



I2

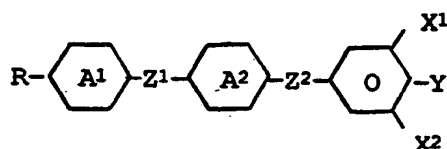
25 In the compounds of the formula I2, R is preferably alkyl or alkoxy having 1-10, but in particular 1-8, C atoms, the straight-chain radicals being preferred. Furthermore, n-alkoxyalkyl compounds and in particular n-alkoxymethyl and n-alkoxyethyl compounds are preferred.

Z^2 is preferably $-\text{CH}_2\text{CH}_2-$, $-\text{COO}-$ or a single bond, in particular a single bond or $-\text{CH}_2\text{CH}_2-$ and very particularly a single bond. Y is $-\text{F}$, $-\text{Cl}$, $-\text{CN}$, $-\text{OCHF}_2$, $-\text{OCF}_3$ or $-\text{CF}_3$, preferably $-\text{F}$, $-\text{Cl}$ or $-\text{CN}$; in case of actively addressed PDLC systems according to the present invention Y is preferably $-\text{F}$, $-\text{Cl}$ or $-\text{OCF}_3$.

Compounds of the formula I2 in which at least one of X^1 and X^2 is different from H are particularly preferred.



A^2 is preferably Cyc, Phe.(F), Phe.3F5F, Phe.2F3F, Pyr, Pyd or Dio and in particular Cyc, Phe.(F), Phe.3F5F, Phe.2F3F, Pyr or Pyd.

Furthermore, electrooptical systems whose liquid crystal mixture contains one or more trinuclear compounds of the formula I3 are preferred:

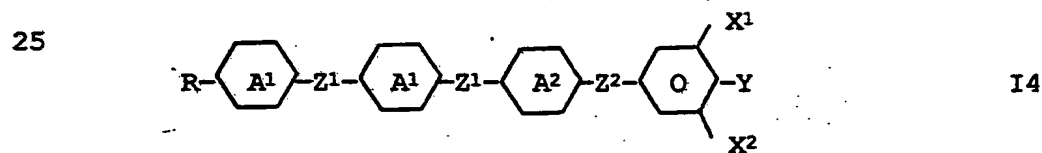


I3

In the compound of the formula I3, R is preferably n-alkyl or n-alkoxy having 1-10 C atoms, furthermore also n-alkoxymethyl or n-alkoxyethyl having 1-8 C atoms and n-alkenyl having up to 7 C atoms.

Very particular preference is given to compounds of the formulae I3 in which R is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, octoxy, methoxymethyl, ethoxymethyl, propoxymethyl, butoxymethyl, methoxyethyl, ethoxyethyl or propoxyethyl. Z¹ and Z² in the compounds of the formulae I3 are, independently of one another, preferably -CH₂CH₂-, -COO- or a single bond and in particular -CH₂CH₂- or a single bond. Particular preference is given to those compounds of the formula I3 in which at least one of Z¹ or Z² is a single bond. Y is -F, -Cl, -CN, -OCHF₂, -OCF₃ or -CF₃ and preferably -F, -Cl, -CN, -OCHF₂ or -OCF₃; in case of actively addressed PDLC systems according to the present invention Y is in particular -F, -Cl, -OCHF₂ and -OCF₃.  and  are, independently of one another, Cyc, Phe.(F), Phe.2F3F, Phe.3F5F, Phe.2F3F5F, Pyr, Pyd and Dio and in particular Cyc, Phe.(F), Phe.2F3F, Phe.3F5F, Phe.2F3F5F, Pyr and Pyd.




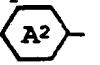
Furthermore, electrooptical systems whose liquid crystal mixture contains one or more tetranuclear compounds of the formula I4 are preferred:



30 In the compounds of the formulae I4, R is preferably n-alkyl or n-alkoxy having 1-10 C atoms, furthermore also n-alkoxymethyl or n-alkoxyethyl having 1-8 C atoms.

Very particular preference is given to compounds of the formulae I4 in which R is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy or octoxy.

5

In the compounds of the formula I4, preferably not more than 2 and in particular only one of the bridges Z¹ and Z² are different from a single bond.  and  are preferably, independently of one another, Cyc, Phe.2F, Phe.3F, Phe, Pyr or Pyd. Compounds of the formula I4 in which at least one of  and  is Phe.2F or Phe.3F are preferred. The weight proportion of the compounds of the formulae I4 in the liquid crystal mixture of the electrooptical systems according to the invention is preferably not too high and is in particular less than 20 %, the use of laterally fluorinated compounds of the formula I4 being in many cases preferred.

The proportion of the compounds of the formula I in the liquid crystal mixtures used according to the invention is preferably not too small and is in particular more than 15 % and very particularly more than 20 %. Liquid crystal mixtures containing more than 40 % and in particular not less than 50 % of compounds of the formula I are particularly preferred.

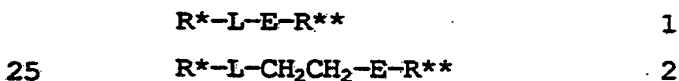
25

The liquid crystal mixtures used according to the invention can contain further components which are preferably selected from nematic or nematogenic (monotropic or isotropic) substances, in particular substances from the group comprising azoxybenzenes, benzylideneanilines, biphenyls, terphenyls,

30

phenyl or cyclohexyl benzoates, phenyl or cyclohexyl cyclohexanecarboxylates, phenyl or cyclohexyl cyclohexylbenzoates, phenyl or cyclohexyl cyclohexylcyclohexanecarboxylates, cyclohexylphenyl benzoate, cyclohexylphenyl cyclohexanecarboxylate, or cyclohexylphenyl cyclohexylcyclohexanecarboxylate, phenylcyclohexanes, cyclohexylbiphenyls, phenylcyclohexylcyclohexanes, cyclohexylcyclohexanes, cyclohexylcyclohexenes, cyclohexylcyclohexylcyclohexenes, 1,4-bis(cyclohexyl)benzenes, 4,4'-bis(cyclohexyl)biphenyls, phenyl- or cyclohexylpyrimidines, phenyl- or cyclohexylpyridines, phenyl- or cyclohexyldioxanes, phenyl- or cyclohexyl-1,3-dithianes, 1,2-diphenylethanes, 1,2-dicyclohexylethanes, 1-phenyl-2-cyclohexylethanes, 1-cyclohexyl-2-(4-phenylcyclohexyl)ethanes, 1-cyclohexyl-2-biphenylylethanes, 1-phenyl-2-cyclohexylphenylethanes, halogenated or unhalogenated stilbenes, benzyl phenyl ethers, tolans and substituted cinnamic acids. The 1,4-phenylene groups in these compounds can also be fluorinated.

The liquid crystal mixtures used in the electrooptical systems according to the invention preferably also contain one or more dielectrically neutral compounds of the formulae 1-5:



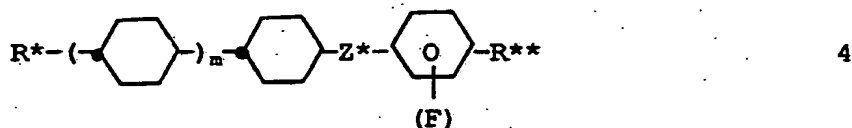
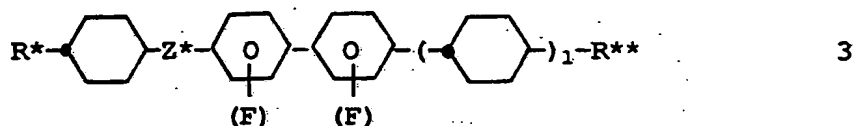
In the formulae 1 and 2 L and E, which may be identical or different, are each, independently of one another, a bivalent radical from the group comprising -Phe-, -Cyc-, -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -Pyr-, -Dio-, -G*-Phe- and -G*-Cyc- and

mirror images thereof, Phe being unsubstituted or fluorine-substituted 1,4-phenylene, Cyc being trans-1,4-cyclohexylene or 1,4-cyclohexenylene, Pyr being pyrimidine-2,5-diyl or pyridine-2,5-diyl, Dio being 1,3-dioxane-2,5-diyl and G* being 2-(trans-1,4-cyclohexyl)ethyl, pyrimidine-2,5-diyl, pyridine-2,5-diyl or 1,3-dioxane-2,5-diyl.

One of the radicals L and E is preferably Cyc, Phe or Pyr. E is preferably Cyc, Phe or Phe-Cyc. The liquid crystals according to the invention preferably contain one or more components selected from compounds of the formulae 1 and 2, in which L and E are selected from the group comprising Cyc, Phe and Pyr and simultaneously one or more components are selected from the compounds of the formulae 1 and 2, in which one of the radicals L and E is selected from the group comprising Cyc, Phe and Pyr and the other radical is selected from the group comprising -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -G*-Phe- and -G*-Cyc-, and, if desired, one or more components are selected from the compounds of the formulae 1 and 2, in which the radicals L and E are selected from the group comprising -Phe-Cyc-, -Cyc-Cyc-, -G*-Phe- and -G*-Cyc-.

R* and R** in the compounds of the formulae 1 and 2 are each, independently of one another, preferably alkyl, alkenyl, alkoxy, alkenyloxy or alkanoyloxy having up to 8 carbon atoms. In most of these compounds, R* and R** are different from one another, one of these radicals being in particular alkyl, alkoxy or alkenyl.

Especially preferred is the following smaller group of dielectrically neutral compounds of formulae 3 and 4



wherein

the meaning of R^* and R^{**} is the same as given for formulae 1 and 2,

15 Z^* is independently from each other a single bond or $-\text{CH}_2\text{CH}_2-$,

1 and m are independently from each other 0 or 1, and

20 $\underset{\text{(F)}}{\text{C}_6\text{H}_4}$ denotes 1,4-phenylene, 2-fluoro-1,4-phenylene or 3-fluoro-1,4-phenylene.

25 The weight proportion of the compounds of the formulae 1-4 in the liquid crystals used according to the invention is preferably 0-50 % and in particular 0-40 %.

30 The liquid crystal mixtures used in the electrooptical systems according to the invention preferably contain 1-98 %, in

particular 5-05 %, of compounds of the formula I. The liquid crystals preferably contain 1-20, but in particular 1-15, and very particularly 1-12, compounds of the formula I.

5 One skilled in the art can select additives for the liquid crystal mixtures described from the large pool of nematic or nematogenic substances in such a manner that the birefringence Δn and/or the ordinary refractive index n_o and/or other refractive indices and/or the viscosity and/or the dielectric
10 anisotropy and/or further parameters of the liquid crystal are optimized with respect to the particular application.

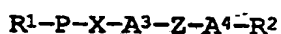
The liquid crystal mixture can contain further additives such as, for example, chiral compounds and other customary addi-
15 tives. The concentration of such additives is preferably not more than 7.5 % and, in particular, lower than 5 %.

Formula II embraces both known and new reactive liquid crystalline compounds, and the present invention also relates to
20 the new reactive liquid crystalline compounds of formula II.

Specifically, the reactive liquid crystalline compounds known so far are often characterized by high or very high melting points and values of the birefringence which are not high
25 enough for many applications.

The present inventors found in extensive investigations that the compounds according to formula III

30



III

wherein

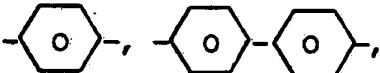
5 R^1 is $CH_2 = CW-COO-$, $CH_2 = CH-$, $HW-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$, $HWN-$, $HS-CH_2-(CH_2)_m-$
 $COO-$ with W being H, Cl or alkyl with 1-5 C atoms and m
 being 1-7,

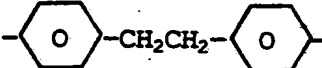
10 P is alkylene with up to 12 C atoms, it being also possible
 for one or more CH_2 groups to be replaced by O,

X is $-O-$, $-S-$, $-COO-$, $-OCO-$ or a single bond,

15 R^2 is alkyl radical with up to 15 C atoms which is unsubsti-
 tuted, mono-or polysubstituted by halogen, it being also
 possible for one or more CH_2 groups in these radicals
 to be replaced, in each case independently of one
 another, by $-O-$, $-S-$, $-CO-$, $-OCO-$, $-CO-O-$ or $-O-CO-O-$ in
 such a manner that oxygen atoms are not linked directly
 to one another, $-CN$, $-F$, $-Cl$ or alternatively R^2 has one
 20 of the meanings given for R^1-Q-X ,

25 A^3 is a 1,4-phenylene or a naphthalene-2,6-diyl radical which
 both can be unsubstituted or substituted with 1 to 4
 halogen atoms, or trans-1,4-cyclohexylene

30 A^4 is (a) , or

(b) 

it being possible for the 1,4-phenylene groups in radicals (a) and (b) to be substituted by CN or halogen and one of the 1,4-phenylene groups in (a) and (b) can also be replaced by a 1,4-phenylene radical in which one or
 5 two CH groups are replaced by N, and

Z is -CO-O-, -O-CO-, -CH₂CH₂- or a single bond,

exhibit favorable properties and, in particular, advantageous
 10 values of birefringence and melting point.

Electrooptical systems according to the present invention the reactive liquid crystalline component of which contains at least one compound according to formula III exhibit especially advantageous properties.
 15

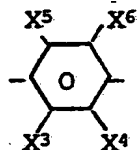
Formula III covers reactive liquid crystalline compounds with 3 rings of formulae III1-III20

20	R ¹ -P-X-Phe'-Z-Phe''-Phe'''-R ²	III1
	R ¹ -P-X-Phe'-Z-Pyd-Phe''-R ²	III2
	R ¹ -P-X-Phe'-Z-Pyr-Phe''-R ²	III3
	R ¹ -P-X-Phe'-Z-Phe''-Pycl-R ²	III4
	R ¹ -P-X-Phe'-Z-Phe''-Pyr-R ²	III5
25	R ¹ -P-X-Phe'-Z-Phe''-CH ₂ CH ₂ -Phe'''-R ²	III6
	R ¹ -P-X-Phe'-Z-Pyd-CH ₂ CH ₂ -Phe'''-R ²	III7
	R ¹ -P-X-Phe'-Z-Pyr-CH ₂ CH ₂ -Phe'''-R ²	III8
	R ¹ -P-X-Phe'-Z-Phe''-CH ₂ CH ₂ -Pyd-R ²	III9
30	R ¹ -P-X-Phe'-Z-Phe''-CH ₂ CH ₂ -Pyr-R ²	III10

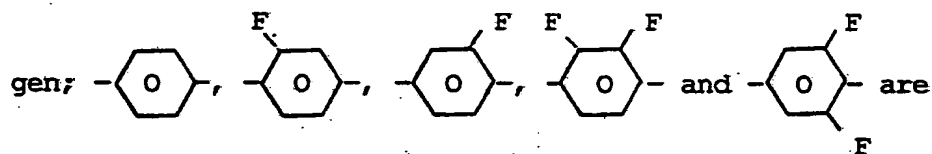
	$R^1-P-X-Nap'-Z-Phe''-Phe''-R^2$	III11
	$R^1-P-X-Nap'-Z-Pyd-Phe''-R^2$	III12
	$R^1-P-X-Nap'-Z-Pyr-Phe''-R^2$	III13
	$R^1-P-X-Nap'-Z-Phe''-Pyd-R^2$	III14
5	$R^1-P-X-Nap'-Z-Phe''-Pyr-R^2$	III15
	$R^1-P-X-Nap'-Z-Phe''-CH_2CH_2-Phe''-R^2$	III16
	$R^1-P-X-Nap'-Z-Pyd-CH_2CH_2-Phe''-R^2$	III17
	$R^1-P-X-Nap'-Z-Pyr-CH_2CH_2-Phe''-R^2$	III18
	$R^1-P-X-Nap'-Z-Phe''-CH_2CH_2-Pyd-R^2$	III19
10	$R^1-P-X-Nap'-Z-Phe''-CH_2CH_2-Pyr-R^2$	III20

In the compounds of formulae III1-III10, Phe' denotes a 1,4-phenylene group

15



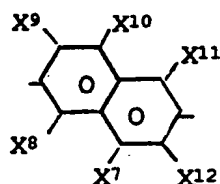
20 wherein X³-X⁶ denote independently from each other H or halo-



25 preferred.

30

In the compounds of formulae IIII1-III22, Phe'' is a 1,4-phenylene group, which is unsubstituted or mono- or polysubstituted by CN or halogen, and in formulae IIII5-III20, Nap' is a naphthalene-2,6-diyl group



which is unsubstituted or wherein up to 4 of X7-X12 are independently from each other halogen while the other denote H.

The compounds of formulae IIII1-III20 are preferred. Especially preferred are the compounds of formulae IIII1-III3, III6-III10, III13-III15, III18-III20, III21 and III22 and, in particular the compounds of formulae IIII1, III8, III15 and III20.

In the compounds of formulae IIII1-III20 R¹ is CH₂ = CW-COO-,
 $\text{CH}_2 = \text{CH}-$, $\text{HW}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$, HWN-, HS-CH₂-(CH₂)_m-COO- with W being H, Cl or alkyl with 1-5 C atoms and m being 1-7.

Preferably, R¹ is a vinyl group, an acrylate group, an amino group or a mercapto group, and especially preferred are the following meanings of R¹:



R¹-1

	$\begin{array}{c} \text{CH}_2=\text{C}-\text{COO}- \\ \\ \text{CH}_3 \end{array}$	R ¹ -2
5	$\begin{array}{c} \text{CH}_2=\text{C}-\text{COO}- \\ \\ \text{Cl} \end{array}$	R ¹ -3
	$\text{CH}_2=\text{CH}-$	R ¹ -4
	$\text{H}_2\text{N}-$	R ¹ -5
10	$\text{H(alkyl)N}-$	R ¹ -6
	$\text{HS}-\text{CH}_2-(\text{CH}_2)_m-\text{COO}-$	R ¹ -7

with alkyl denoting C₁-C₃-alkyl and m being 1-5.

- 15 In the compounds of formulae III1-III20, the spacer-type group P is alkylene with up to 24 C atoms, it is also being possible for one or more non adjacent CH₂ groups to be replaced by O.
- 20 In case P is alkylene, P may be straight-chain or branched. P especially preferred is ethylene, propylene, butylene, 1-methyl-propylene, 2-methyl-propylene, pentylene, 1-methyl-butylene, 2-methyl-butylene, hexylene, 2-ethyl-butylene, 1,3-dimethyl-butylene, heptylene, 1-methylhexylene, 2-methylhexylene,
- 25 lene, 3-methylhexylene, 4-methylhexylene, 5-methylhexylene, 6-methylhexylene, octylene, 3-ethyl-hexylene, nonylene, 1-methyloctylene, 2-methyloctylene, 7-methyloctylene, decylene, undecylene, dodecylene, 2-methylundecylene, 2,7,5-trimethyl-nonylene or 3-propyl-nonylene.
- 30

In case P is mono- or polyoxaalkylene, P may be straight-chain or branched. In particular, P is 1-oxa-ethylene, 1-oxa-propylene, 2-oxapropylene, 1-oxa-butylene, 2-oxabutylene, 1,3-dioxabutylene, 1-oxa-pentylene, 2-oxa-pentylene, 3-oxy-pentylene, 2-oxa-3-methyl-butylene, 1-oxahexylene, 2-oxa-hexylene, 3-oxa-hexylene, 1,3-dioxa-hexylene, 1,4-dioxy-hexylene, 1,5-dioxa-hexylene, 1-oxy-heptylene, 2-oxa-heptylene, 1,3-dioxa-heptylene, 1,4-dioxa-heptylene, 1,5-dioxa-heptylene, 1,6-dioxa-heptylene, 1,3,5-trioxa-heptylene, 1-oxa-octylene, 2-oxa-octylene, 3-oxa-octylene, 4-oxa-octylene, 1,3-dioxaoctylene, 1,4-dioxa-nonylene, 1,4-dioxa-decylene, 1,4-dioxa-undecylene and 1,3,5-trioxa-dodecylene.

X is -O-, -S-, -COO-, -OCO- or a single bond and in particular -O-, -COO-, -OCC- or a single bond. In case X is -O-, -S- or -OCO-, the adjacent CH₂-group of Q is not replaced by -O-.

Z is -COO-, -OCO-, -CH₂CH₂- or a single bond. In the compounds of formulae III1-III7 and III15-III19, Z preferably is -COO-, -OCO-, -CH₂CH₂- or a single bond and, in particular, -COO-, -OCO- or a single bond. In the compounds of formulae III8-III14 and III20-III24, Z preferably is -CH₂CH₂- or a single bond.

R² can be an alkyl radical with up to 15 C atoms which is unsubstituted, mono- or polysubstituted by halogen, it also being possible for one or more CH₂ groups in these radicals to be replaced, in each case independently from one another, by -O-, -S-, -CO-, -OCO-, -COO- or -O-COO- in such a manner that oxygen atoms are not linked directly to one another.

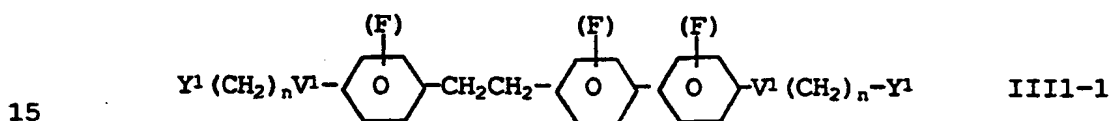
- If R^2 is an alkyl radical or alkoxy radical, it may be straight-chain or branched. Preferably, it is straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy or octoxy, and furthermore methyl, nonyl, decyl, undecyl, tridecyl, tetradecyl, pentadecyl, methoxy, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy.
- 10 If R^2 is oxaalkyl, it is preferably straight-chain 2-oxapropyl (= methoxymethyl), 2-oxabutyl (= ethoxymethyl) or 3-oxabutyl (= 2-methoxyethyl), 2-, 3- or 4-oxapentyl, 2-, 3-, 4- or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl, 2-, 3-, 4-, 5-, 6-, 7-, 8-, or 9-oxadecyl.

Preferred branched radicals R^2 are isopropyl, 2-butyl (= 1-methylpropyl), isobutyl (= 2-methylpropyl), 2-methylbutyl, isopentyl (= 3-methylbutyl), 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, 2-octyl, isopropoxy, 2-methylpropoxy, 2-methylbutoxy, 3-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy, 2-octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methylpentyl, 4-methylhexyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methyloctoxy, 6-methyloctanyloxy, 5-methylheptyloxycarbonyl, 2-methylbutyryloxy, 3-methylvaleryloxy, 4-methylhexanoyloxy, 2-chloropropionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-methylvaleryloxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxy-pentyl, 2-methyl-3-oxahexyl.

R² can also be a polar terminal group and in particular -CN, -Cl or -F; R² can also be -(L)-C_dH_eF_{1,d+1-e} wherein L is a single bond -O- or -S-, d is 1 or 2 and e is 0, 1, 2, 3, 4 or 5.

5 R² can also have one of the meanings given for R¹-Q-X- above. In case R² is an - optionally substituted - alkyl radical, R¹ preferable is a vinyl or acrylate group while in case R² is R¹-Q-X, all meanings given above for R¹ are preferred.

10 Especially preferred is the following smaller group of reactive liquid crystalline compounds according to formula IIII1:



wherein

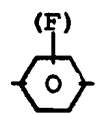
20 Y¹ is independently from each other CH₂=C(W¹)COO-, CH₂=CH- or HS-CH₂-(CH₂)_mCOO-,

V¹ is independently from each other -O-, -COO-, -OOC-, -S- or a single bond,


W¹ is independently from each other H, Cl or CH₃,

25 n is independently from each other 2-12,


m is independently from each other 1-7, and

30  is independently from each other 1,4-phenylene, 2-fluoro-1,4-phenylene, 3-fluoro-1,4-phenylene, 2,6-difluoro-1,4-phenylene or 2,3,6-trifluoro-1,4-phenylene.

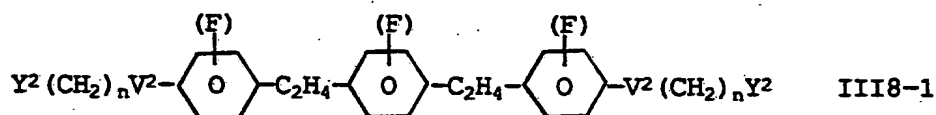
The compounds according to formula III-1 may be laterally

unsubstituted (all groups  denote 1,4-phenylene) or 1, 2 or 3 1,4-phenylene groups may be substituted independently from each other by 1, 2 or 3 F atoms. Laterally fluorinated compounds are preferred.

Especially preferred are compounds according to formula

IIII-1 wherein Y^1 is $CH_2=CHCOO$, V^1 is O and  is independently from each other 1,4-phenylene or 2-fluoro- or 3-fluoro-1,4-phenylene. The compounds of this smaller subclass of compounds according to formula IIII-1 are characterized by advantageous values of birefringence and by low melting points.

Especially preferred is also the following smaller group of compounds according to formula IIII8:

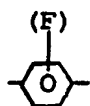


wherein

Y^2 is independently from each other $CH_2=CHCOO-$, $CH_2=C(CH_3)-COO-$ or $CH_2=CH-$,

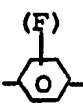
V^2 is independently from each other $-O-$ or a single bond,

n is independently from each other 2-12, and



has the meaning indicated for IIII-1.

5

The compounds according to this formula may be laterally
unsubstituted (all groups ) denote 1,4-phenylene) or 1, 2
or 3 1,4-phenylene groups may be substituted independently
from each other by 1, 2 or 3 F atoms. Laterally fluorinated
compounds are preferred.

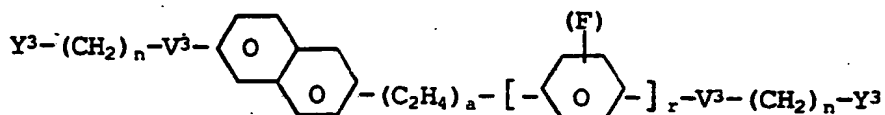
10

Especially preferred are compounds according to formula
III8-1 wherein Y¹ is CH₂=CH-COO- and V² is -O-. The compounds
according to formula III8-1 exhibit especially advantageous
melting points.

15

Especially preferred are further compounds according to the
following formula

20



wherein

25

Y³ is independently from each other CH₂=CW³COO-, CH₂=CH-
or HSCH₂(CH₂)_m-COO-,

V³

is independently from each other -O-, -COO-, -OOC-,
-S- or a single bond,

W³

is independently from each other H, Cl or CH₃,

30

a

is 0 or 1,

n

is independently from each other 2-12,

r is 1 or 2,
 m is independently from each other 1-7, and



has the meaning indicated for III1-1.

Compounds of this type are partially covered by formula III11
 $(r = 2)$. Particularly preferred are compounds of this type

wherein

Y^3 is $CH_2=CW^3COO-$

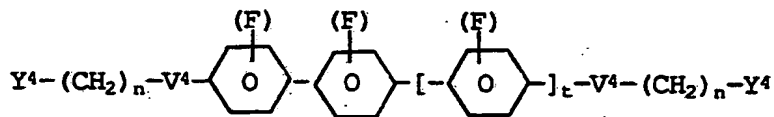
n is independently from each other 3-11 and in particular
 4, 5, 6, 7 or 8,

V^3 is $-O-$ or a single bond, and

r is 1.

The compounds of this specific subgroup are characterized by
 advantageous values of the melting point and the birefrin-
 gence.

Especially preferred is further the following smaller group
 of reactive liquid crystalline compounds according to the
 following formula



wherein

- 58 -

Y⁴ is independently from each other CH₂=CW⁴COO-, CH₂=CH-
or HSCH₂(CH₂)_mCOO-,

V⁴ is independently from each other -O-, -COO-, -OCO-,
-S- or a single bond,

5

W⁴ is independently from each other H, CH₃ or Cl,

m is independently from each other 1-7,

n is independently from each other 1-12,


t is 0, 1 or 2, and

10



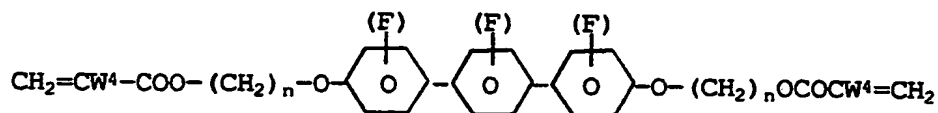
has the meaning indicated for IIII-1. Compounds of
this type are partly covered by formula IIII.

15 The compounds according to this formula may be laterally

unsubstituted (all groups  denote 1,4-phenylene) or 1, 2
or 3 1,4-phenylene groups may be substituted independently
from each other by 1, 2 or 3 F atoms. Laterally fluorinated
20 compounds are preferred.

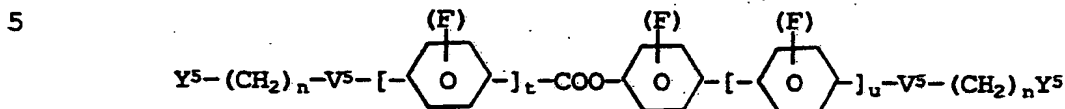
Particularly preferred is the following rather small group of
compounds:

25



The compounds of this specific subgroup are characterized by
advantageous values of the melting point and the birefrin-
30 gence.

Especially preferred is further the following smaller group of reactive liquid crystalline compounds according to the following formula

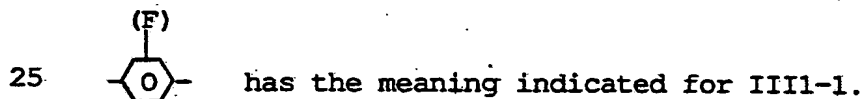


wherein

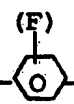
- 10 Y^5 is independently from each other $CH_2=CW^5COO-$, $CH_2=CH-$ or $HSCH_2(CH_2)_mCOO$,
 V^5 is independently from each other $-O-$, $-COO-$, $-OCO-$, $-S-$ or a single bond,
 15 W^5 is independently from each other H, CH_3 or Cl,
 n is independently from each other 1-12,
 m is 1-7,

t and u are independently from each other 0, 1 or 2 with the proviso that $t+u = 1, 2$ or 3 ,
 20

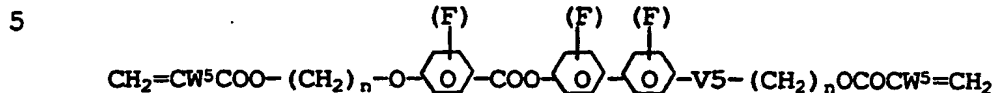
and



The compounds according to formula III-1 may be laterally

30 unsubstituted (all groups  denote 1,4-phenylene) or 1, 2 or 3 1,4-phenylene groups may be substituted independently from each other by 1, 2 or 3 F atoms. Laterally fluorinated compounds are preferred.

Compounds of this type are partly covered by formula III1.
Particularly preferred in the following rather small group of
compounds:



Especially preferred is further the following smaller group
of compounds:

10



wherein

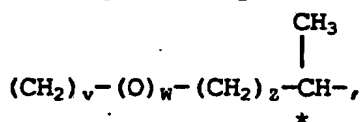
15

Y^6 is independently from each other $\text{CH}_2=\text{CW}^6\text{COO}-$, $\text{CH}_2=\text{CH}-$
or $\text{HSCH}_2(\text{CH}_2)_m\text{COO}-$,

W^6 is independently from each other H, CH_3 or Cl

T^6 is independently from each other straight chain $(\text{CH}_2)_n$ or

20



m is independently from each other 1-7,

n is independently from each other 1-12,

25

v is independently from each other 1-8,

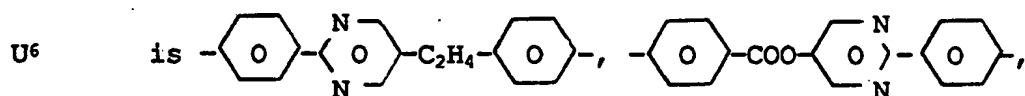
w is independently from each other 0 or 1,

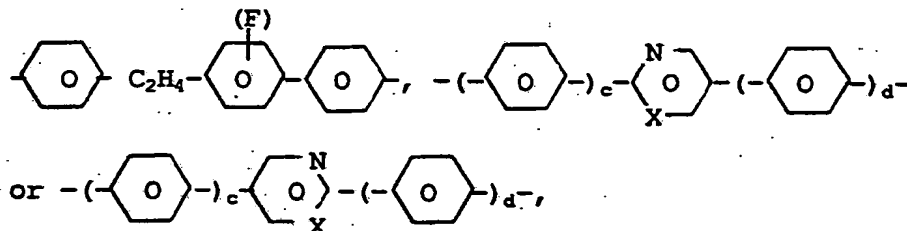
z is independently from each other 0-4,

V^6 is independently from each other $-\text{O}-$, $-\text{S}-$, $-\text{COO}-$,
 $-\text{OCO}-$ or a single bond and,

30

in particular, $-\text{O}-$ or $-\text{S}-$





c and d are independently from each other 0, 1 or 2,
c+d is 1, 2 or 3,
X is N or CH, and



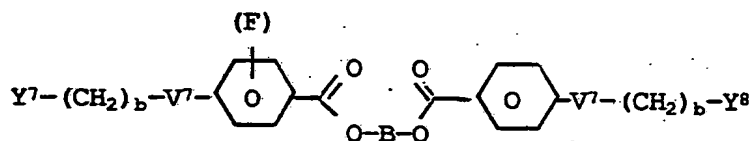
has the meaning indicated for III1-1.

The compounds of this specific subclass are characterized by advantageous values of the melting point and the birefrin-



gence. Compounds wherein T⁶ is (CH₂)_v-(O)_w-(CH₂)_z-CH-O- are optically active.

Especially preferred is further the following smaller group of reactive liquid crystalline compounds



wherein

Y⁷ is CH₂=CW⁷COO-, CH₂=CH-, HSCH₂(CH₂)_mCOO-,

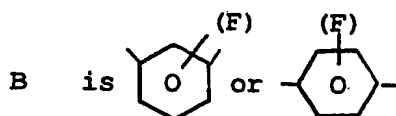
Y⁸ has independently of Y⁷ the meaning of Y⁷ or is an alkyl group with 1-12 C atoms, which is optionally mono- or polysubstituted by F and/or Cl, and/or wherein one or two non-adjacent CH₂ groups may be replaced by -CH=CH-, -O-, -CO-, -COO-, -OCO- or -S-,

V⁷ is independently from each other -O-, -COO-, -OOC-, -S- or a single bond,

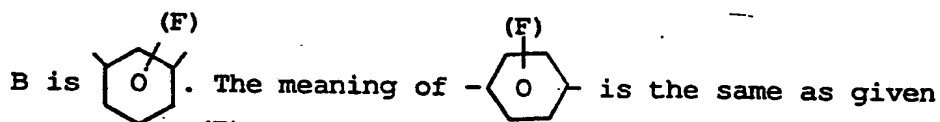
W⁷ is independently from each other H, Cl or CH₃,

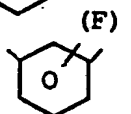
m is independently from each other 1-7,

b is independently from each other 0-11, and



with the proviso that in case both Y⁷ and Y⁸ are CH₂=CW⁷COO-,



above.  comprises all isomers of mono- and difluorinated 1,3-phenylene.

The reactive liquid crystalline compounds according to formula I and, in particular, the preferred compounds according to formula III and according to the preferred subclasses can be prepared by methods which are known per se and which are described, for example, in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der Organischen Chemie, Thieme-Verlag, Stuttgart. Some specific methods can be taken from the examples.

In the following and in the preceding, all percentages given are percentages by weight. Temperatures are given in degrees Celsius.

- 5 The following examples are intended to illustrate the invention without restricting it.

Example 1

- 10 The reactive liquid crystalline compounds (1)



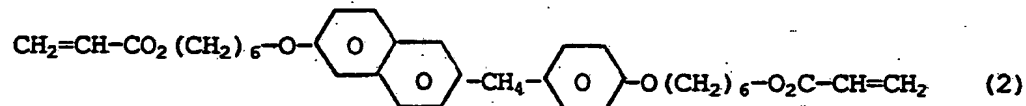
- 15 is prepared via the sequence of reaction steps shown in diagram 1. Pd(Ph)₃ tetrakis triphenylphosphine palladium and Δ denotes heating.

- 20 In step 6 of diagram 1, 1 mol of the phenylether obtained in step 5 and 1.1 mol of acryloyl chloride are dissolved in 1 l of dichloromethane. 1.1 mol of triethylamine are added, and the mixture is stirred for 3 hours at room temperature. Aqueous work-up and column chromatography gives (1).

Example 2

25

The reactive liquid crystalline compound (2)



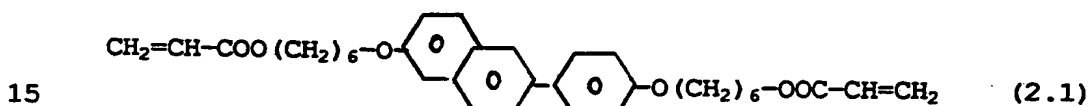
30

is prepared via the sequence of reaction steps shown in diagram 2. TEA is triethylamine, DCM is dichloromethane and rt is room temperature.

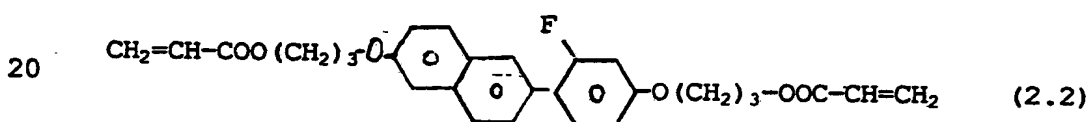
- 5 In step 4 of diagram 2, 2.2 mol of triethylamine is added dropwise to a mixture of 1 mol of the alcohol obtained in step 3, and 2.1 mol of acryloyl chlorid in 2 l of dichloromethane. After 24 hours the reaction mixture is washed with water, and volume chromatography gives (2).

10

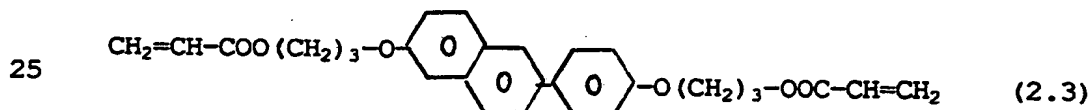
The following compound are prepared via the sequence of reaction steps shown in diagram 2a.



K 80.1 S (66.3) S_A 111.9 I

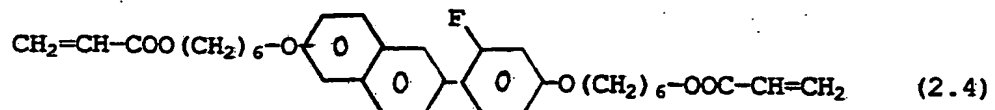


K 60.5 I



K 80.8 S_A 113.8 I

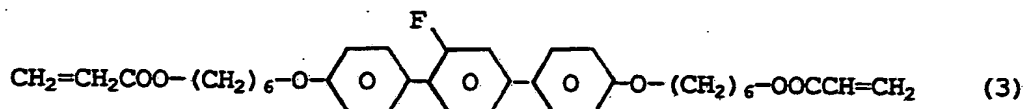
30



K 65 (S_A 61.1 N 63) I

Example 3

The reactive liquid crystalline compound (3)

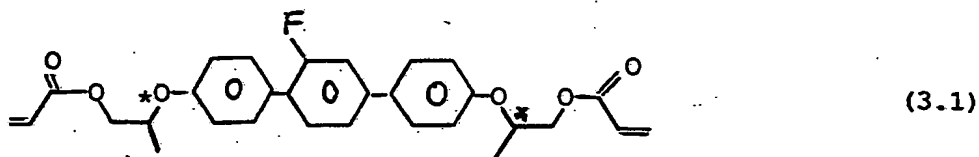


is prepared via the sequence of reaction steps shown in diagram 3 and exhibits the following phase sequence: K 70 S_A 140 I.

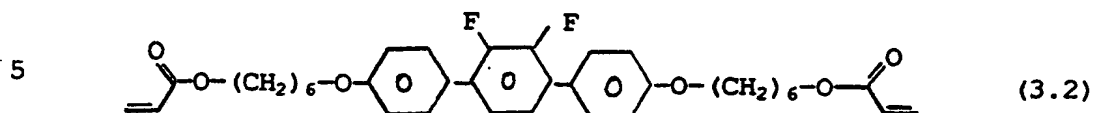
DME is dimethoxyethane.

In step 5 of diagram 3 2.2 mol of triethylamine is added dropwise to a solution of 1 mol of the hydroxyterphenyl obtained in step 4 of diagram 3, and 2.1 mol acryloyl chloride in 2 l dichloromethane. It is stirred for 4 hours at room temperature. Aqueous work-up and column chromatography gives (3).

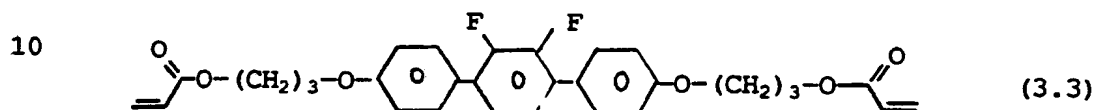
The following compounds are prepared analogously.



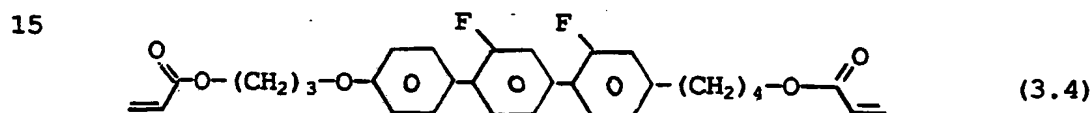
(3.1) exhibits the following phase sequence: K 82.3 I. The carbon atoms denoted by *, are chiral; (R) (-).



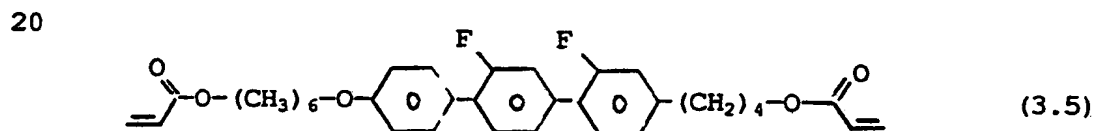
(3.2) exhibits the following phase sequence: K 76.9 S 122.7 I



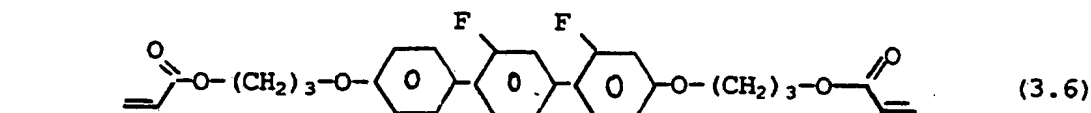
Melting point of (3.3): K 93 S.



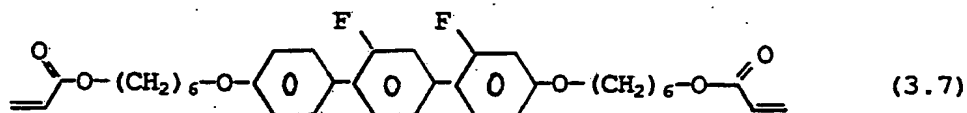
(3.4) exhibits the following phase sequence: K 62 N 81.9 I.



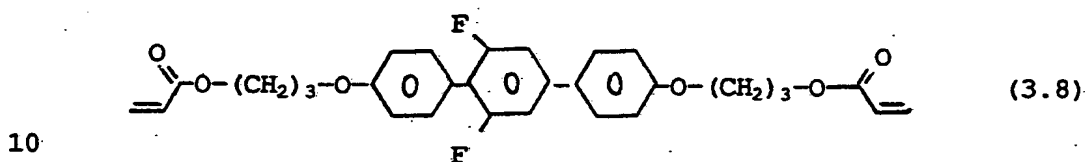
(3.5) exhibits the following phase sequence: K 36.2 S 54.6 N 79.6 I.



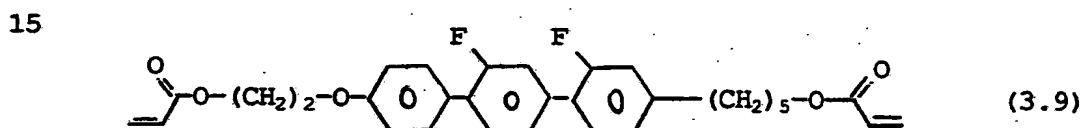
30 (3.6) exhibits the following phase sequence: K 94 N 106 I.



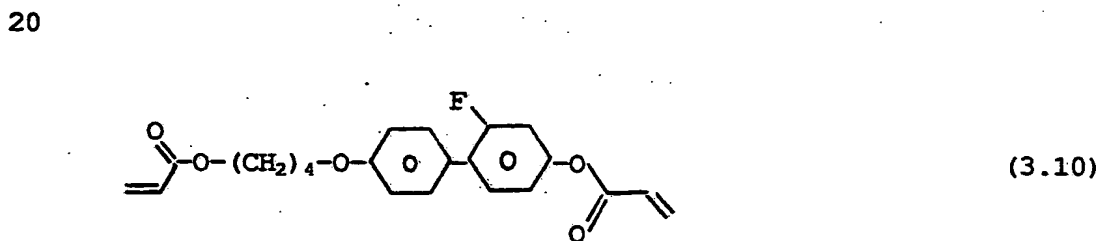
5 (3.7) exhibits the following phase sequence: K 75.3 S 96.9 N 104.9 I.



10 (3.8) exhibits the following phase sequence: K 99.3 N 102.6 I.



15 (3.9) exhibits the following phase sequence: K 67 I.



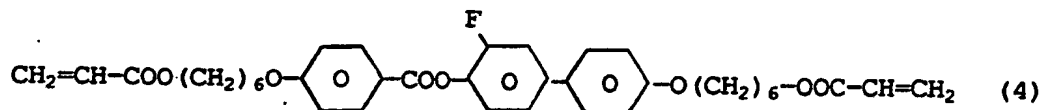
25 (3.10) exhibits the following phase sequence: K 45.6 I.

30

Example 4

The reactive liquid crystalline compound (4)

5



is prepared via the sequence of reaction steps shown in diagram 4.

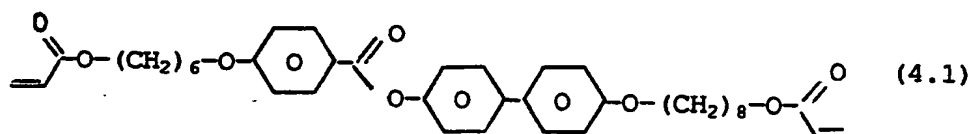
10

In step 4 of diagram 4, 2.2 mol triethylamine is added drop-wise to a solution of the ester obtained in step 3 of diagram 4, and 2.1 mol acryloyl chloride in 2 l dichloromethane. The reaction mixture is stirred at room temperature for 4 hours. Aqueous work-up and column chromatography gives (4).

15

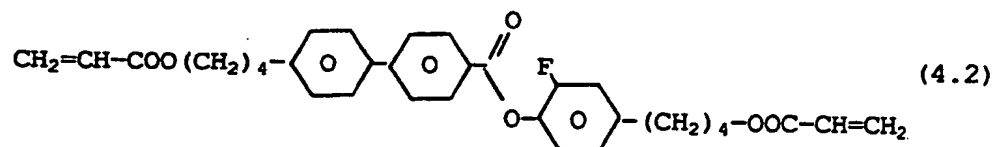
The following compounds are prepared analogously.

20



(4.1) exhibits the following phase sequence: K 87 S_A 145 N 170 I.

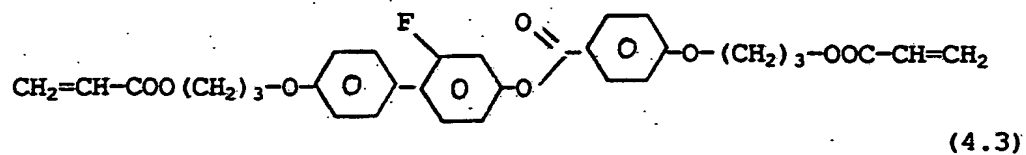
25



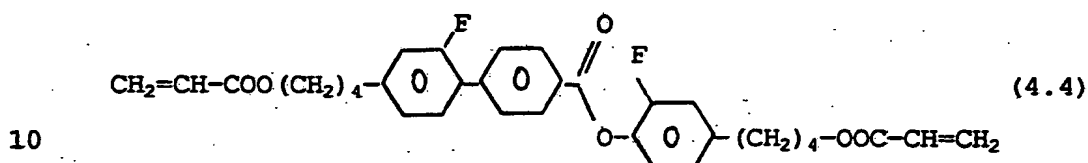
30

(4.2) exhibits the following phase sequence: K 44.4 S_A 70.2 N 104.5 I.

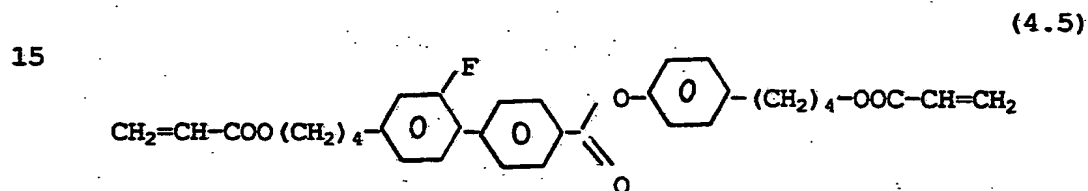
- 69 -



5 (4.3) exhibits the following phase sequence: K 68 N 133 I.



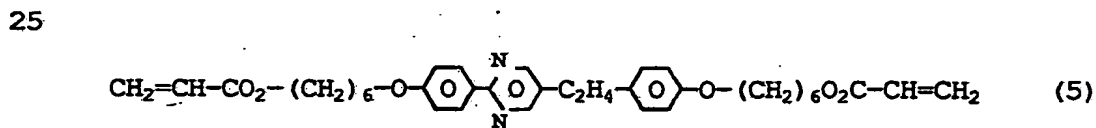
10 (4.4) exhibits the following phase sequence: K 45.7 N 75.4 I.



15 (4.5) exhibits the following phase sequence: K 49.9 N 89.7 I.

Example 5

The reactive liquid crystalline compound (5)



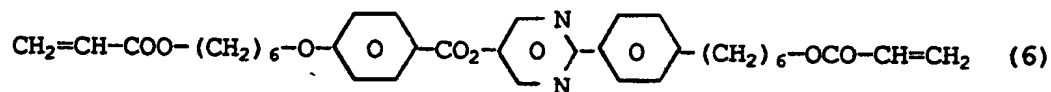
25 is prepared via the sequence of reaction steps shown in
30 diagram 5.

- 70 -

In step 4, 2.2 mol of triethylamine is added dropwise to a solution of 1 mol of the substituted pyrimidine obtained in step 3 of diagram 5, and 2.1 mol of acryloyl chloride in 2 l dichloromethane. The reaction mixture is stirred at room temperature for 4 hours. Aqueous work-up and column chromatographic gives (5).

Example 6

The reactive liquid crystalline compound (6)



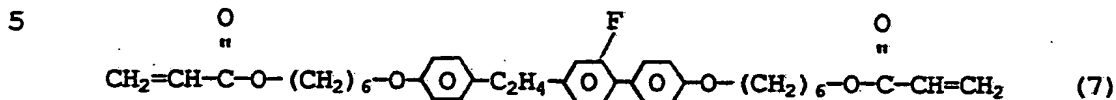
is prepared via the sequence of reaction steps shown in diagram 6.

Buli is buytyllithium and B(OMe)₃ is trimethylborate.

In step 4, 2.2 mol of triethylamine is added dropwise to a solution of 1 mol of the substituted pyrimidine obtained in step 3 of diagram 6, and 2.1 mol of acryloyl chloride in 2 l dichloromethane, and the reaction mixture is stirred at room temperature for 4 hours. Aqueous work-up and column chromatographic gives (6).

Example 7

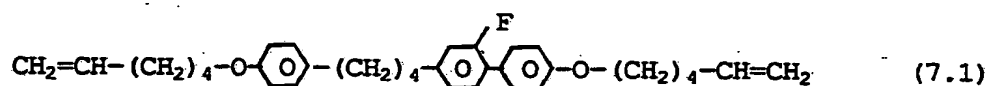
The reactive liquid crystalline compound (7)



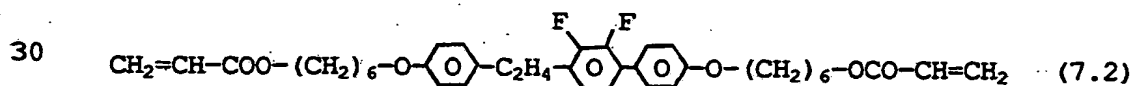
10 is prepared via the sequence of reaction steps shown in diagram 7, and exhibits the following phase sequence: K 39 S 58 S' 85 I (the symmetry of the smectic phases was not determined).

15 In step 4, 2.2 mol of triethylamine is added dropwise to a solution of 1 mol of the ethylene linked compound obtained in step 3 of diagram 4, and 2.1 mol of acryloyl chloride in 2 l dichloromethane. The reaction mixture is stirred for 4 hours at room temperature. Aqueous work-up and column chromatography gives (7).

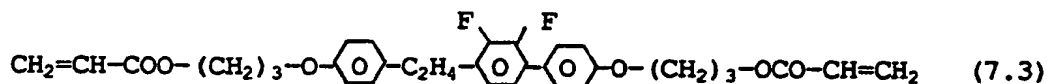
20 The following compounds are prepared analogously.



(7.1) exhibits the following phase sequence: K 58 S 80 S' 107 I (the symmetry of the smectic phases was not determined).



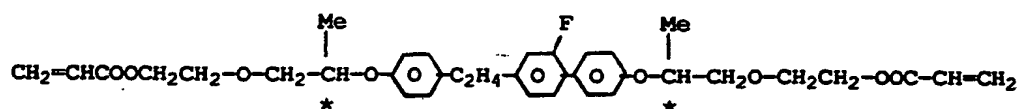
(7.2) exhibits the following phase sequence: K 53 S_A 79.4 I.



(7.3) exhibits the following phase sequence: K 55 S 57 N 62 I.

Example 8

The optically active reactive liquid crystalline compound (8)



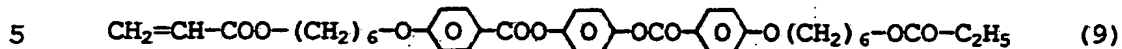
is prepared via the sequence of reaction steps shown in diagram 8.

THF is tetrahydrofuran and Br-CH₂-CH₂-THP is 2-bromo-1-(tetrahydropyranyl)-ethanol which can be prepared according to the method described in A. Hoppmann, Tetrahedron, 34 (1978), 1723.

In step 5, 2.2 mol of triethylamine is added dropwise to a solution of 1 mol of the diol obtained in step 4 of diagram 8, and 2.1 mol of acryloyl chloride in 2 l dichloromethane. The reaction mixture is stirred at room temperature for 4 hours. Aqueous work-up and column chromatography gives (8).

Example 9

The reactive liquid crystalline compound (9)



is prepared via the sequence of reaction steps shown in diagram 9.

10 Et_3N is $(\text{CH}_3\text{CH}_2)_3 \text{N}$.

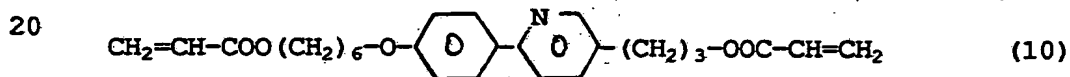
Compound (9) exhibits the following phase sequence:

K 112 N 150 I.

15

Example 10

The reactive liquid crystalline compound (10)



is prepared via the sequence of reaction steps shown in diagram 10.

25

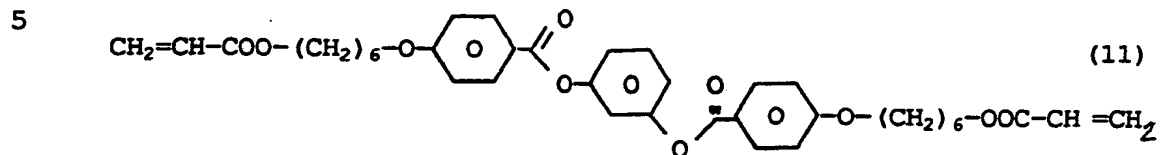
Compound (10) exhibits the following phase sequence:

K 58 (S 39) I.

30

Example 11

The reactive liquid crystalline compound (11)



10 is prepared via the sequence of reaction steps shown in diagram 11.

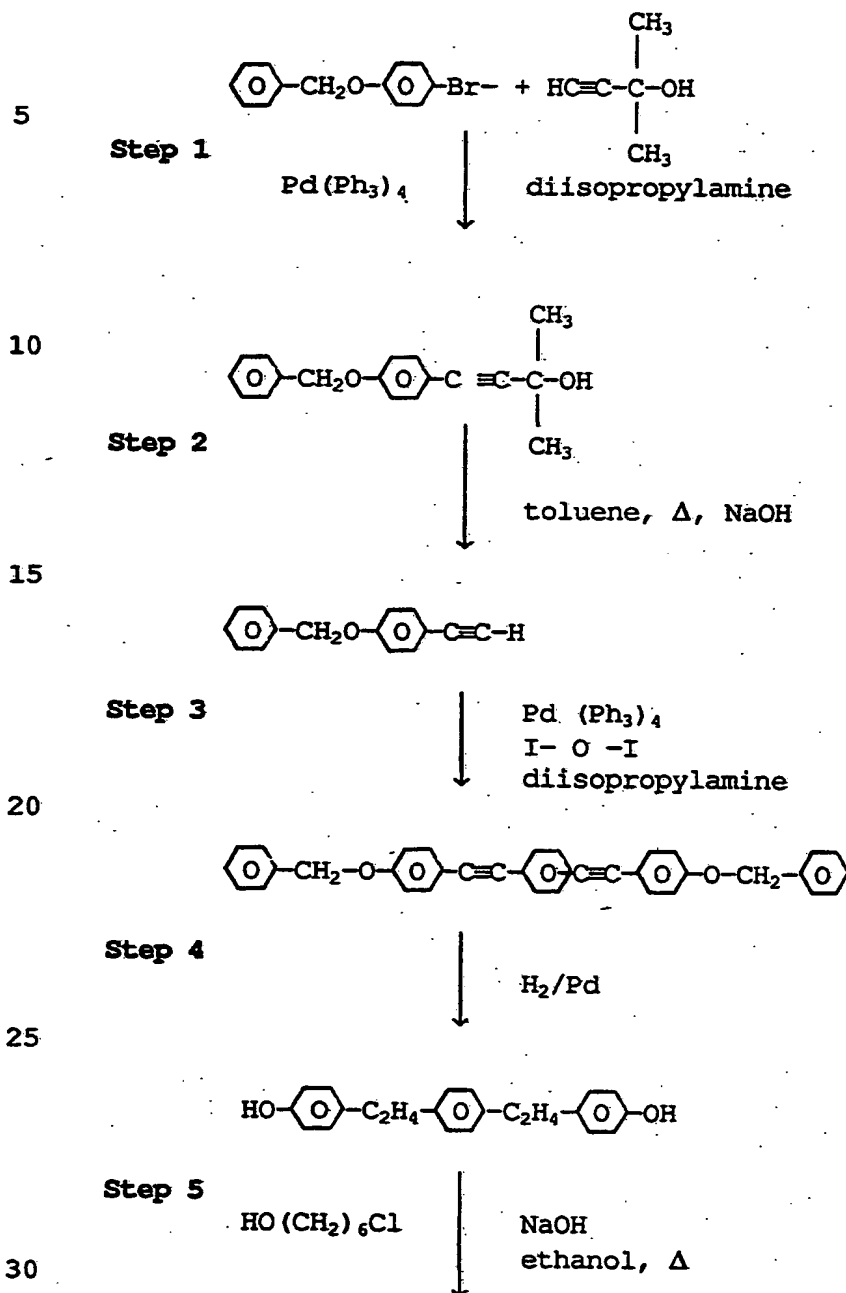
Compound (11) exhibits the following phase sequence:

15 K 48.7 I.

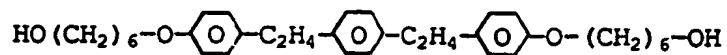
20

25

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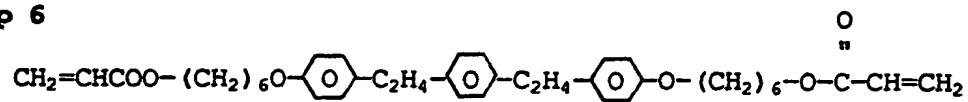
Diagram 1

- 76 -



acryloyl chloride
triethylamine

5

Step 6

10

15

20

25

30

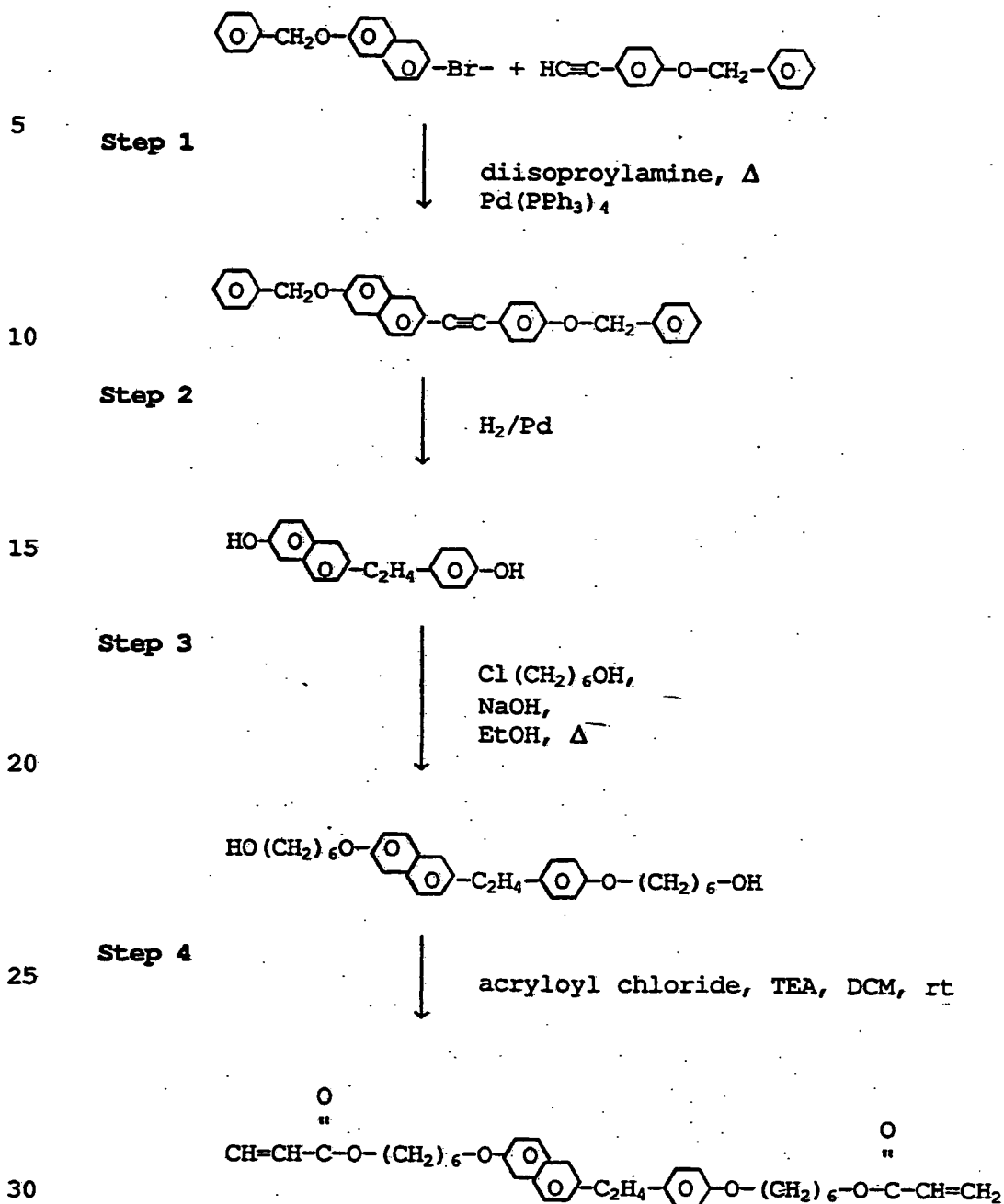
Diagram 2

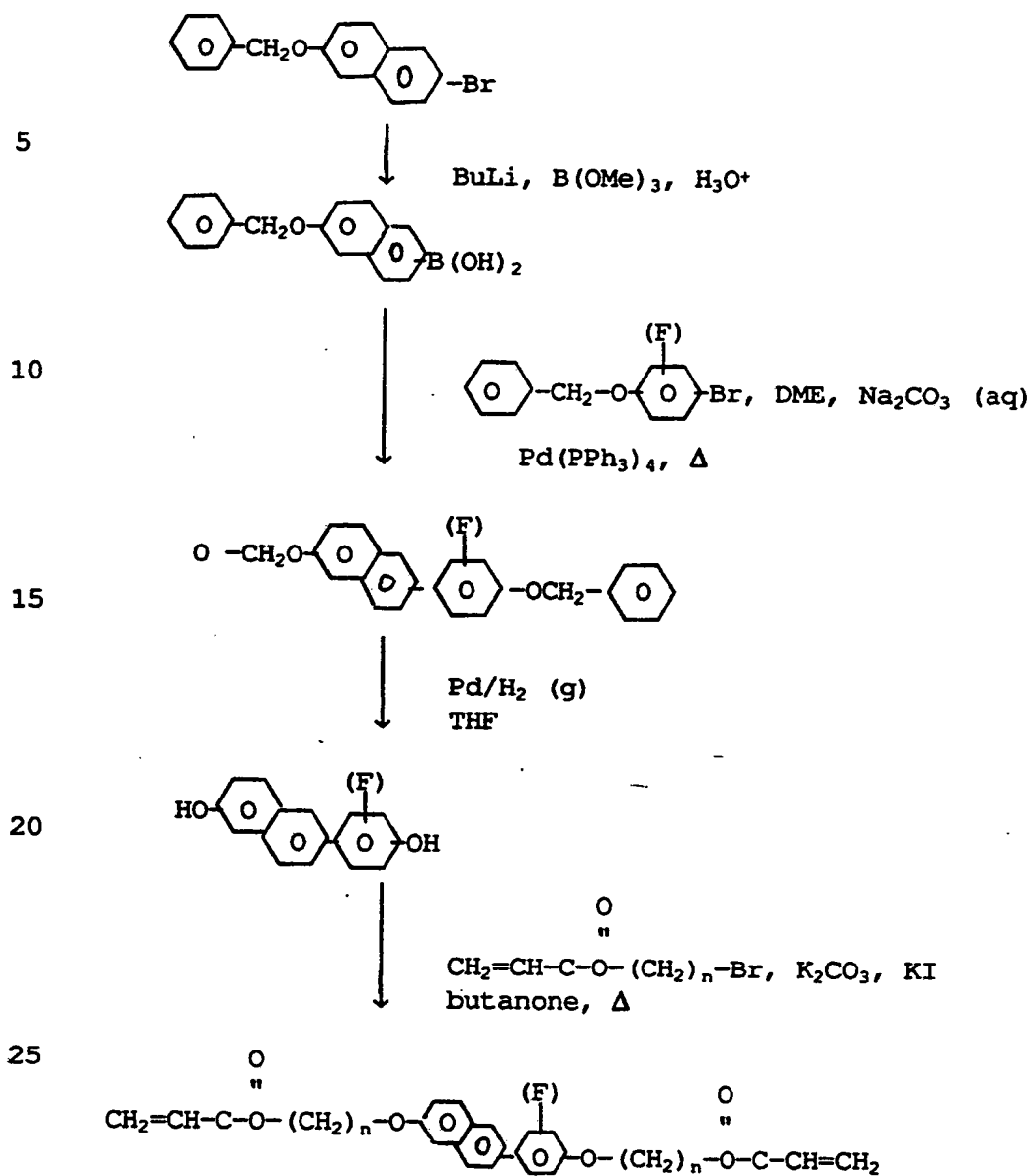
Diagram 2a

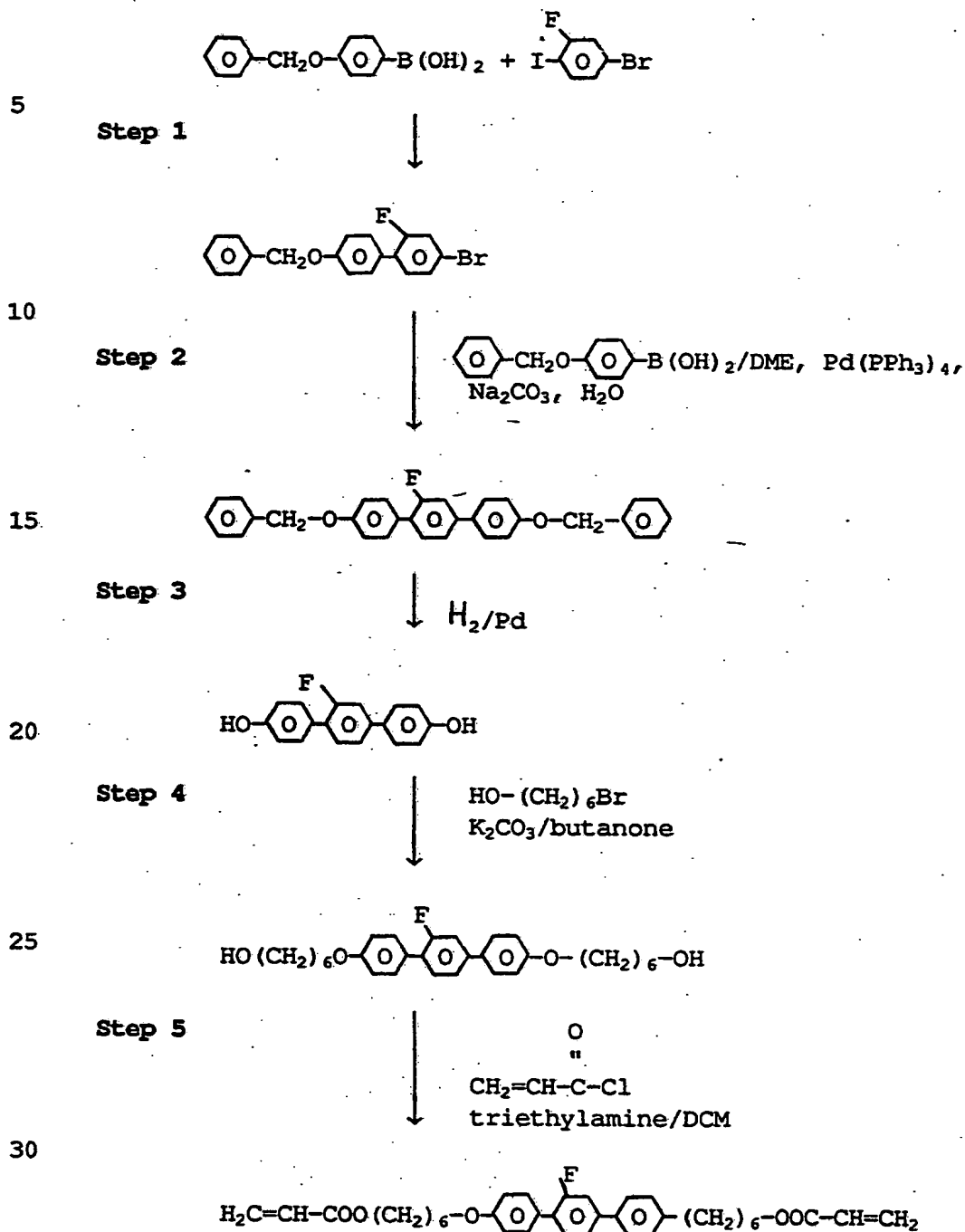
Diagram 3

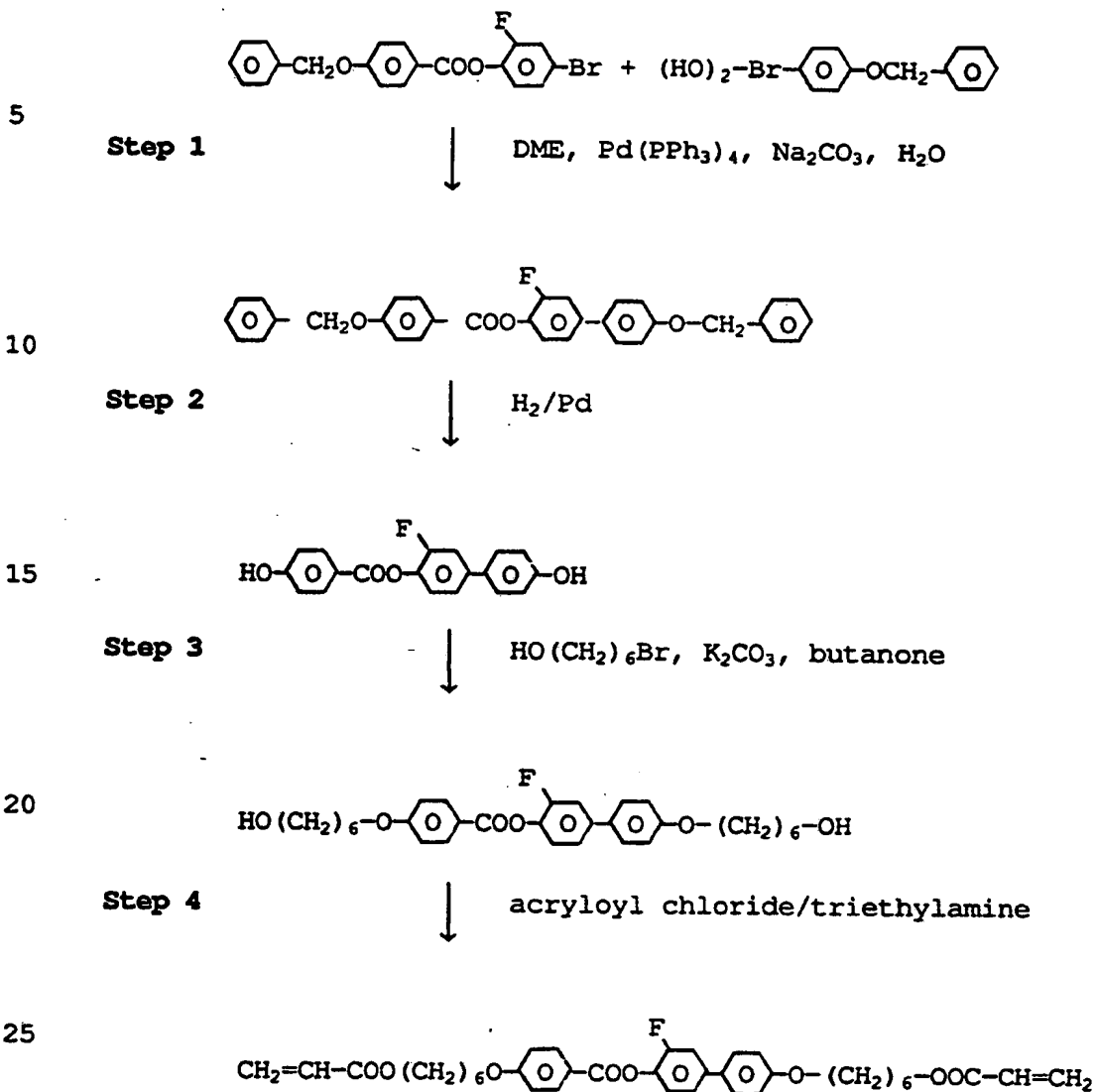
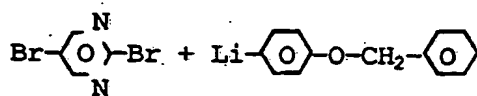
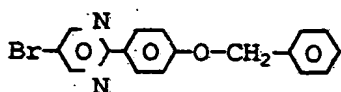
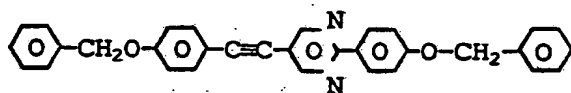
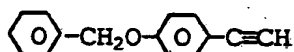
Diagram 4

Diagram 5

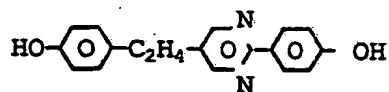
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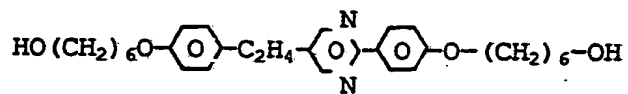
10

Step 1

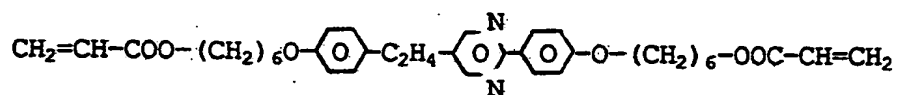
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Step 2 H_2 

20

Step 3

25

Step 4

30

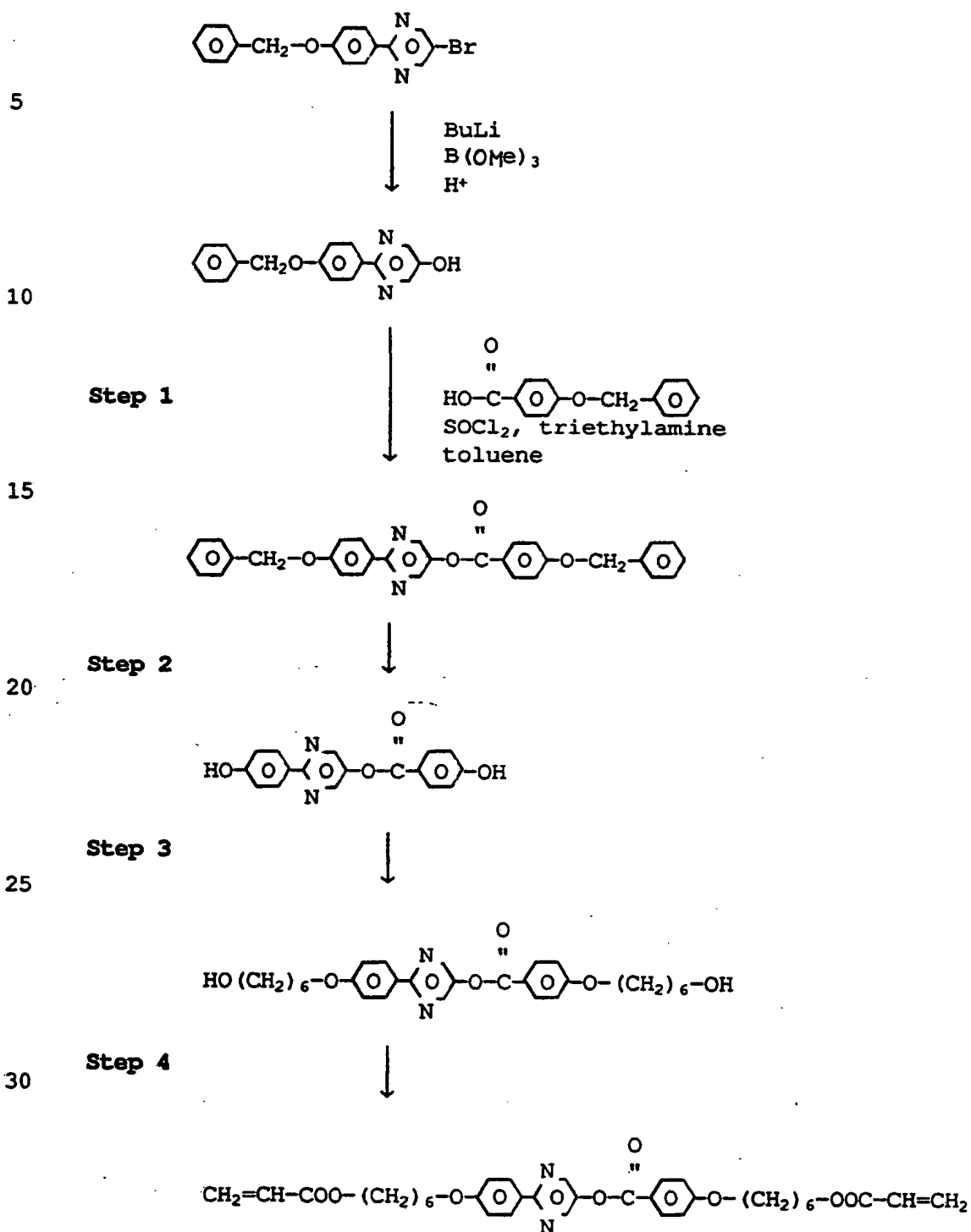
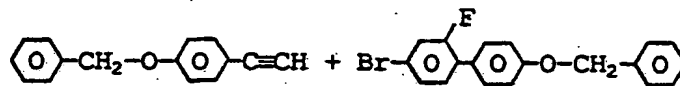
Diagram 6

Diagram 7

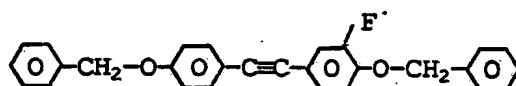
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Step 1

Pd(PPh₃)₄, diisopropylamine/Δ

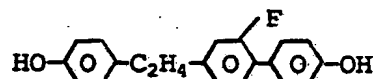
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Step 2

H₂/Pd

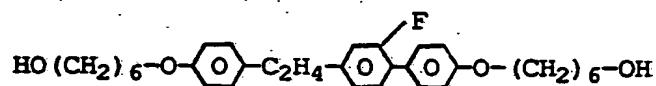
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Step 3

HO(CH₂)₆-Br/K₂CO₃

20

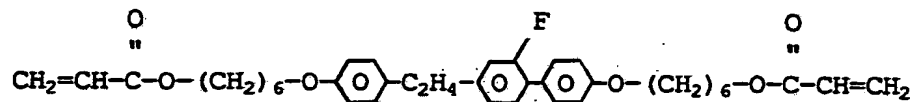


Step 4



acryloyl chloride/triethylamine

25



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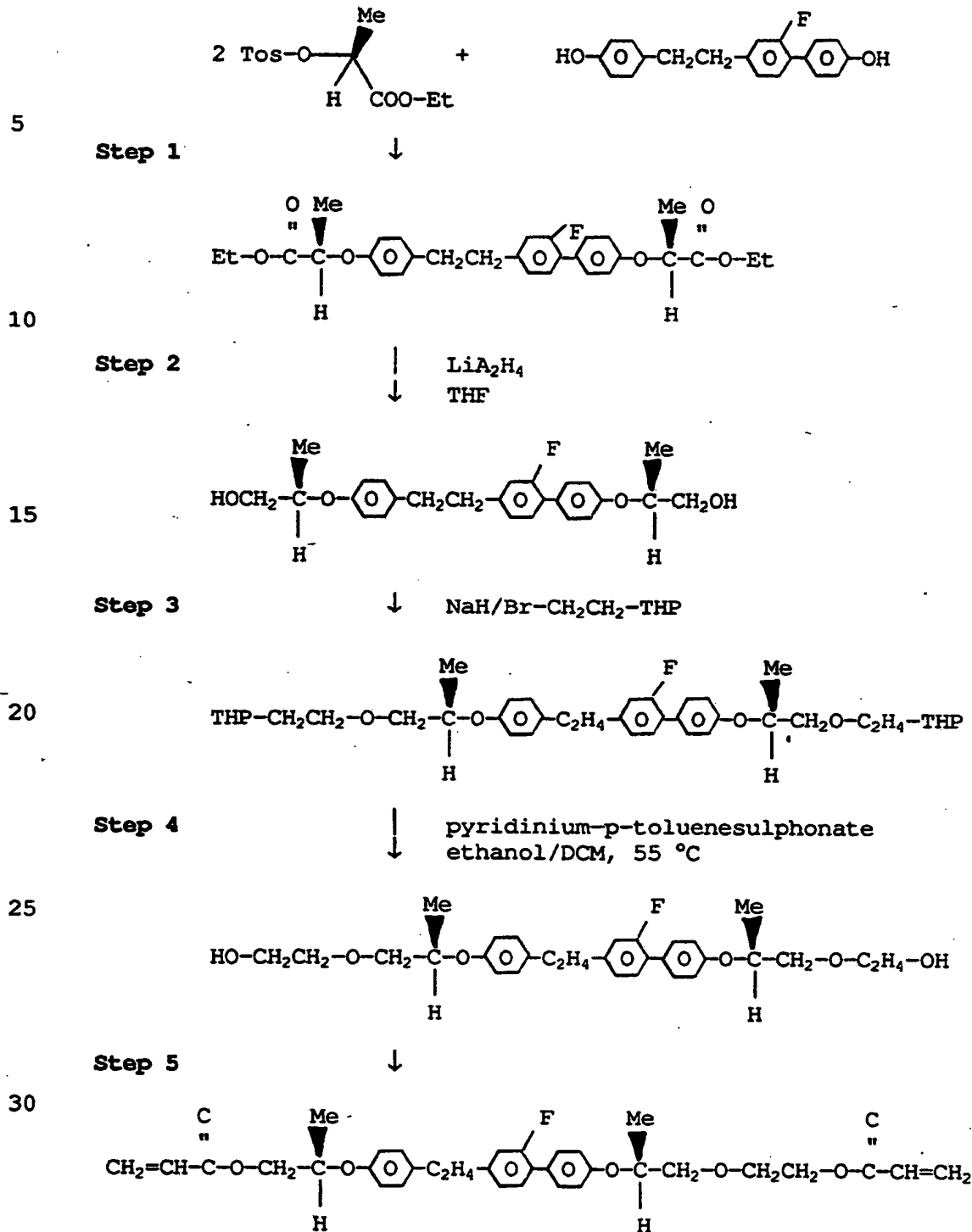
Diagram 8

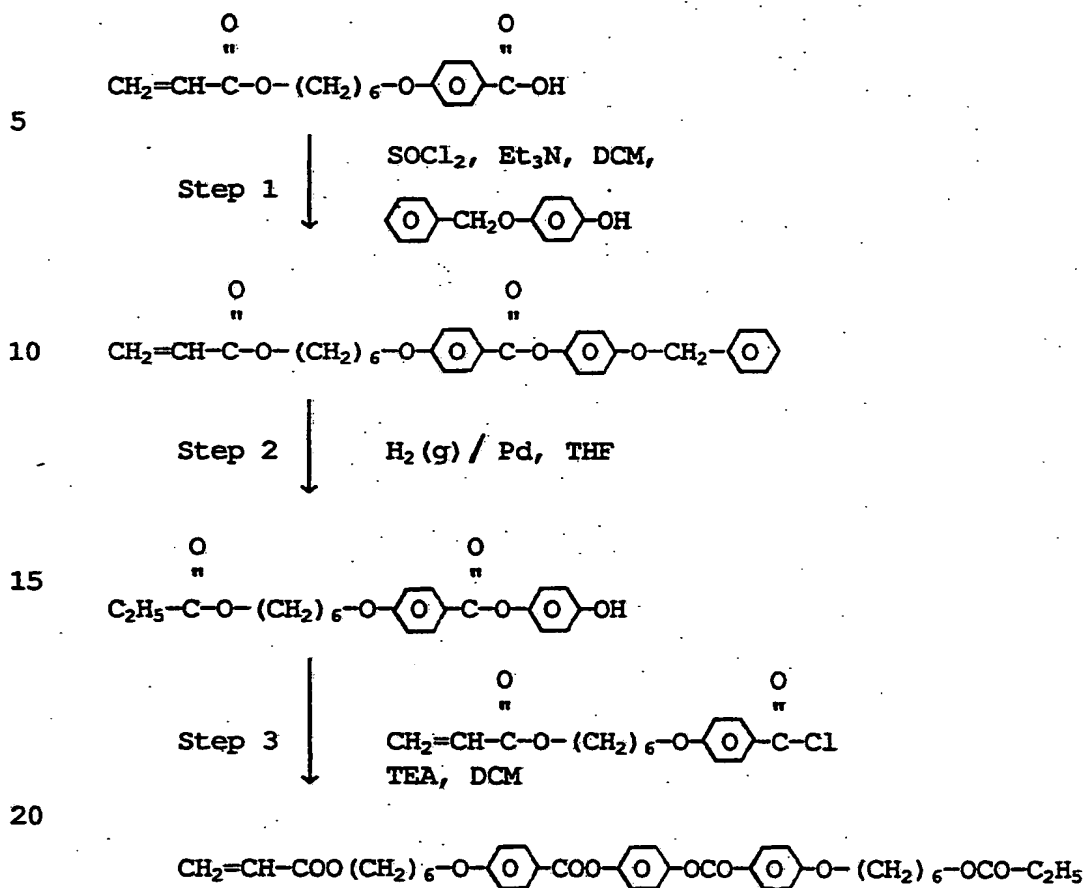
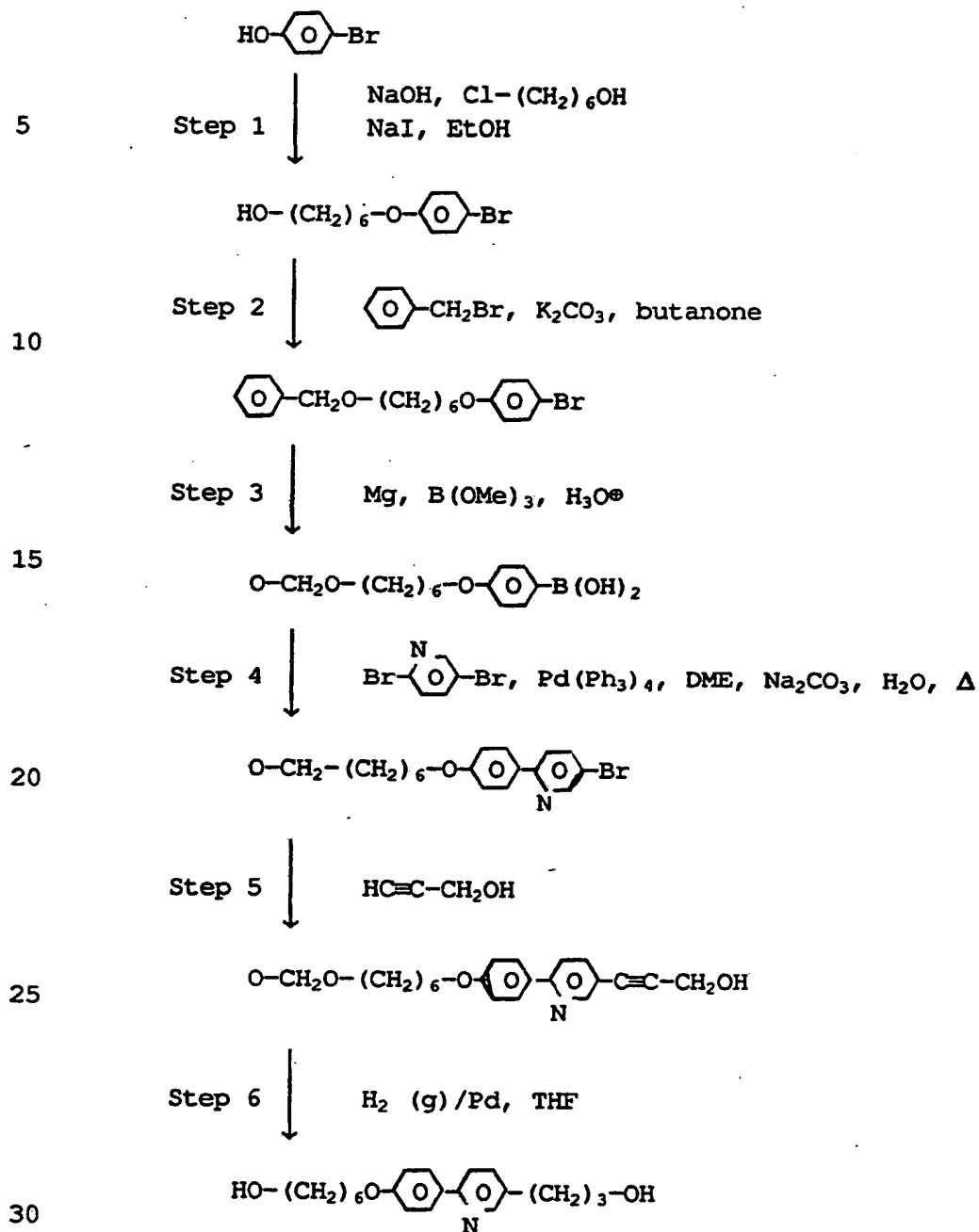
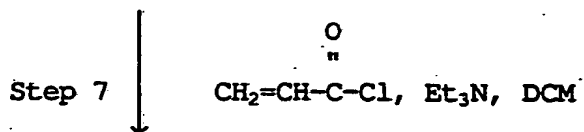
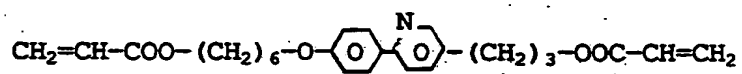
Diagram 9

Diagram 10



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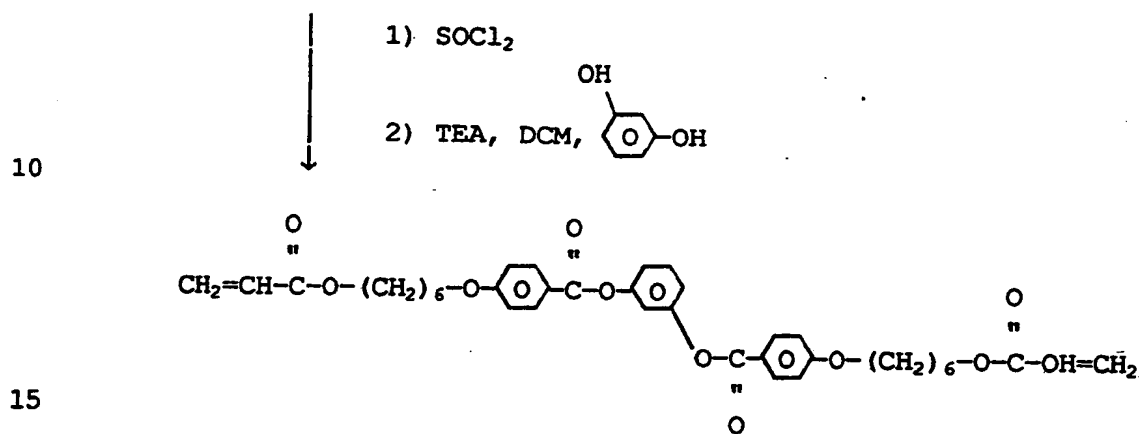
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Diagram 11

$\text{CH}_2=\text{CH}-\text{COO}-(\text{CH}_2)_6-\text{O}-\text{C}_6\text{H}_4-\text{COOH}$ (prepared by the method described
in D.J. Broer, J. Boven, G.N. Moll, G. Challa; Makromol.
Chem. (1982) 183 2311)



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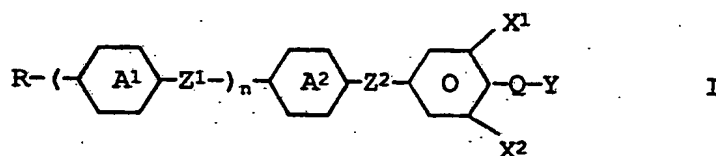
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Patent claims

1. Electrooptical system

- 5 - which between 2 electrode layers contains a PDLC film comprising a liquid crystal mixture forming micro-droplets in an optically isotropic, transparent polymer matrix,
- 10 - in which one of the refractive indices of the liquid crystal mixture is matched to the refractive index of the polymer matrix,
- 15 - which exhibits an electrically switchable transparency essentially independent of the polarization of the incident light,
- 20 - the precursor of the PDLC film of which comprises one or more monomers, oligomers and/or prepolymers and a photoinitiator, and is cured photoradically,
- the liquid crystal mixture of which comprises one or more compounds of the formula I

25



30

in which

Z^1 and Z^2 , independently of one another, are a single bond, $-\text{CH}_2\text{CH}_2-$, $-\text{COO}-$, $-\text{OCO}-$ or $-\text{C}\equiv\text{C}-$,

5 $-\text{A}^1-$ and $-\text{A}^2-$, independently of one another, are trans-1,4-cyclohexylene, 1,4-phenylene, 2-fluoro-1,4-phenylene, 3-fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene or 3,5-difluoro-1,4-phenylene and one of $-\text{A}^1-$ and $-\text{A}^2-$ may also be pyrimidine-2,5-diyl, pyridine-2,5-diyl or trans-1,3-dioxane-2,5-diyl,

X^1 and X^2 , independently from one another, are H or F,

10 Q is $-\text{CF}_2$, $-\text{OCF}_2$, $-\text{C}_2\text{F}_4$, $-\text{OC}_2\text{F}_4$ or a single bond,

Y is $-\text{H}$, $-\text{F}$, $-\text{Cl}$ or $-\text{CN}$,

15 n is 0, 1 or 2 and

R is alkyl having up to 13 C atoms, in which one or two non-adjacent CH_2 groups can also be replaced by $-\text{O}-$ and/or $-\text{CH}=\text{CH}-$

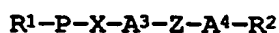
20 characterized in that the liquid crystal mixture additionally contains one or more reactive liquid crystalline compounds in order to obtain improved switching times especially at low temperatures.

25 2. Electrooptical system according to claim 1, containing at least one reactive liquid crystalline compound according to claim 2.

30 3. Electrooptical system according to claim 1 or 2, wherein the mass ratio of the reactive liquid crystalline compound or compounds amounts to 0.01-5 % wt. with respect to the mass of the liquid crystalline mixture.


4. Actively addressed electrooptical system according to claims 1-3, wherein the liquid crystal mixture is being based on SFM compounds according to claim 1.
- 5 5. Electrooptical system according to claims 1-3, wherein the liquid crystal mixture is being based on carbonitriles with the provision that the liquid crystal mixture contains at least 6 compounds and/or that the ratio of 3- and 4-ring compounds to 2-ring compounds is not less than
10 0.18.
6. Precursor of a PDLC film comprising
 - 15 a) a photoradically curable precursor of the PDLC film
 - b) a liquid crystalline mixture comprising one or more compounds of formula I, and
 - 20 c) one or more reactive liquid crystalline compounds.
7. Process for preparing an electrooptical system according to the invention, characterized in that the precursor of claim 5 which is optionally being heated to form a clear solution, is capillary filled between 2 substrates being
25 provided with electrode layers, with subsequent irradiation with light of suitable wavelength in order to cure the precursor, or that the precursor is coated onto a substrate optionally provided with an electrode layer with subsequent curing, and that another substrate provided with an electrode is attached to the cured film or
30 that the cured film is removed from the substrate and being arranged between other substrates being provided with electrodes.

8. Reactive liquid crystal compound of the formula III



III

5 wherein

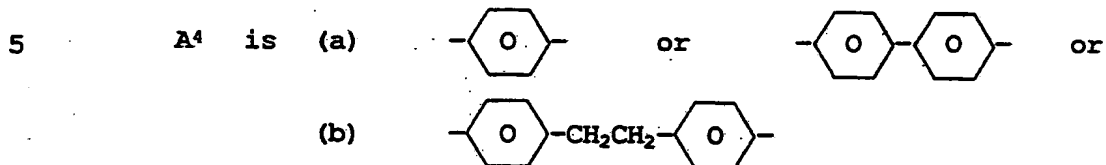
10 R¹ is CH₂=CW-COO-, , HWC-C-, HWN-, CH₂=CH- or HS-CH₂-(CH₂)_m-COO- with W being H, Cl or alkyl with 1-5 C atoms and m being 1-7

15 P is alkylene with up to 12 C atoms, it being also possible for one or more non adjacent CH₂ groups to be replaced by -O-,

X is -O-, -S-, -COO-, -OCO- or a single bond,

20 R² is an alkyl radical with up to 15 C atoms which is unsubstituted, mono- or polysubstituted by halogen, it being also possible for one or more CH₂ groups in these radicals to be replaced, in each case independently of one another, by -O-, -S-, -CO-, -OCO-, -CO-O- or -O-CO-O- in such a manner that oxygen atoms are not linked directly to one another, -CN, -Cl or -F, or alternatively R² has
25 one of the meanings given for R¹-Q-X-,
30

A³ is a 1,4-phenylene or a naphthalene-2,6-diyl radical which both can be unsubstituted or substituted with 1 to 4 halogen atoms,



10 it being possible for the 1,4-phenylene groups in radicals (a) and (b) to be substituted by CN or halogen and one of the 1,4-phenylene groups in (a) and (b) can also be replaced by a 1,4-phenylene radical in which one or two CH groups are replaced by N,

15 and

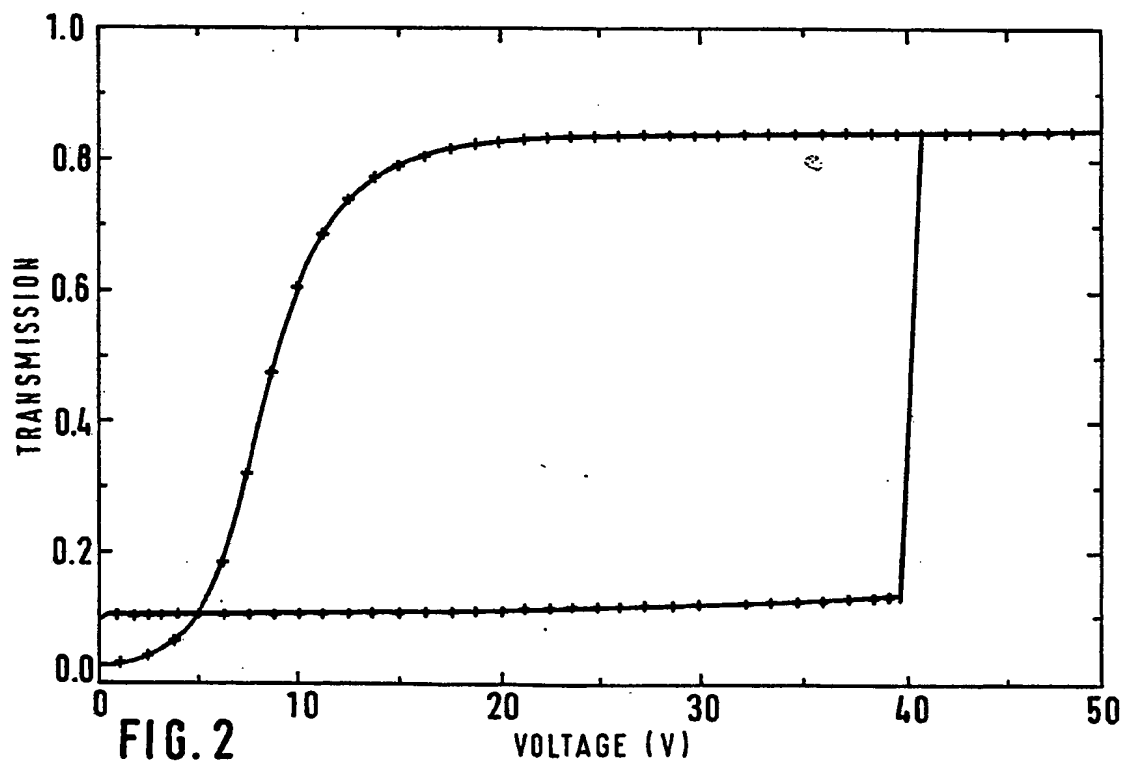
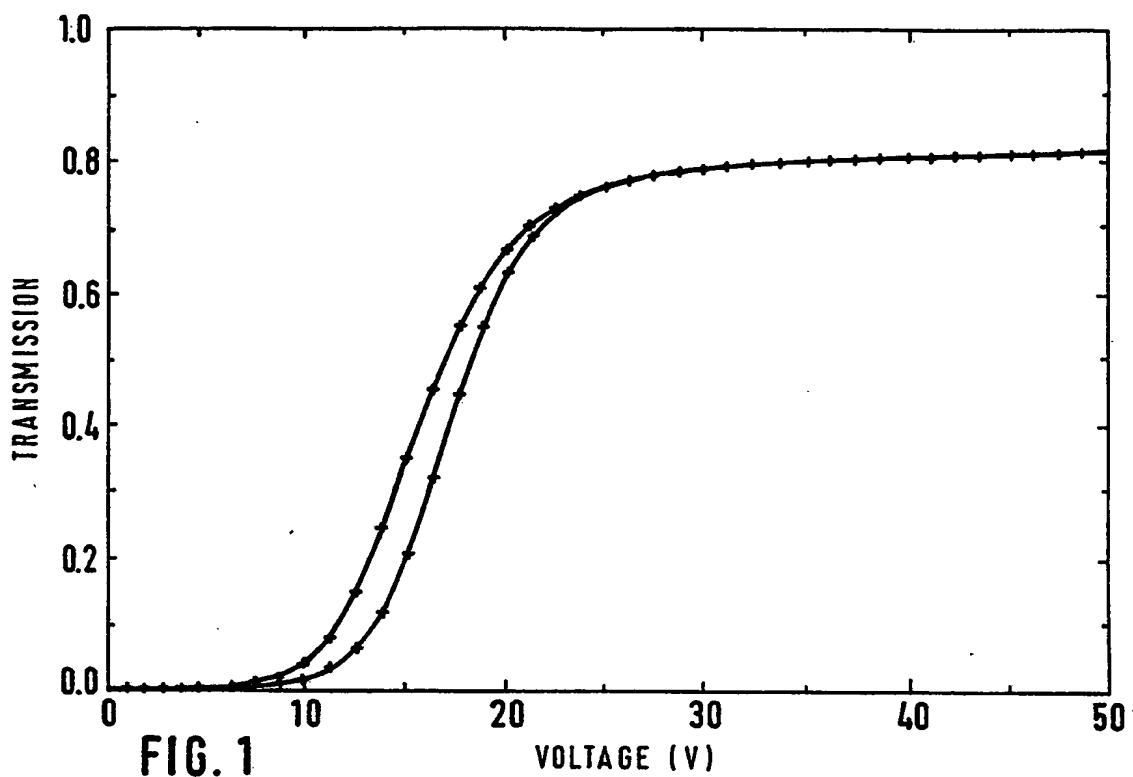
20 Z is -CO-O-, -O-CO-, -CH₂CH₂- or a single bond.

25

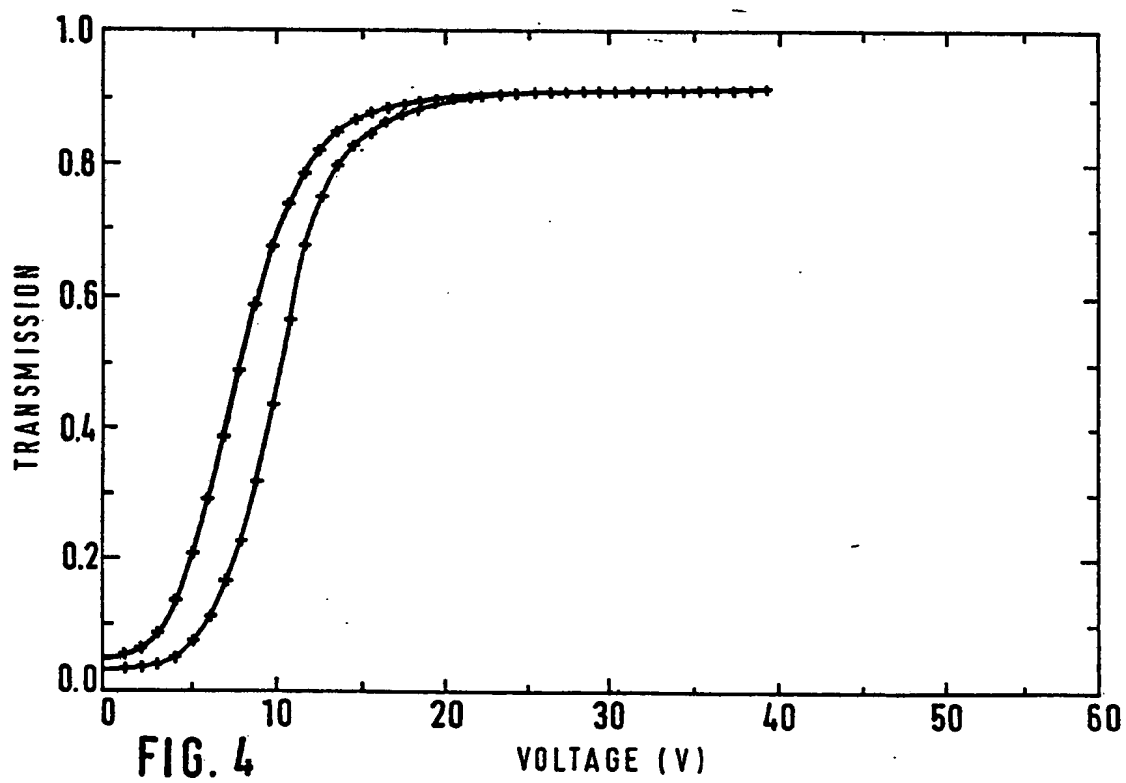
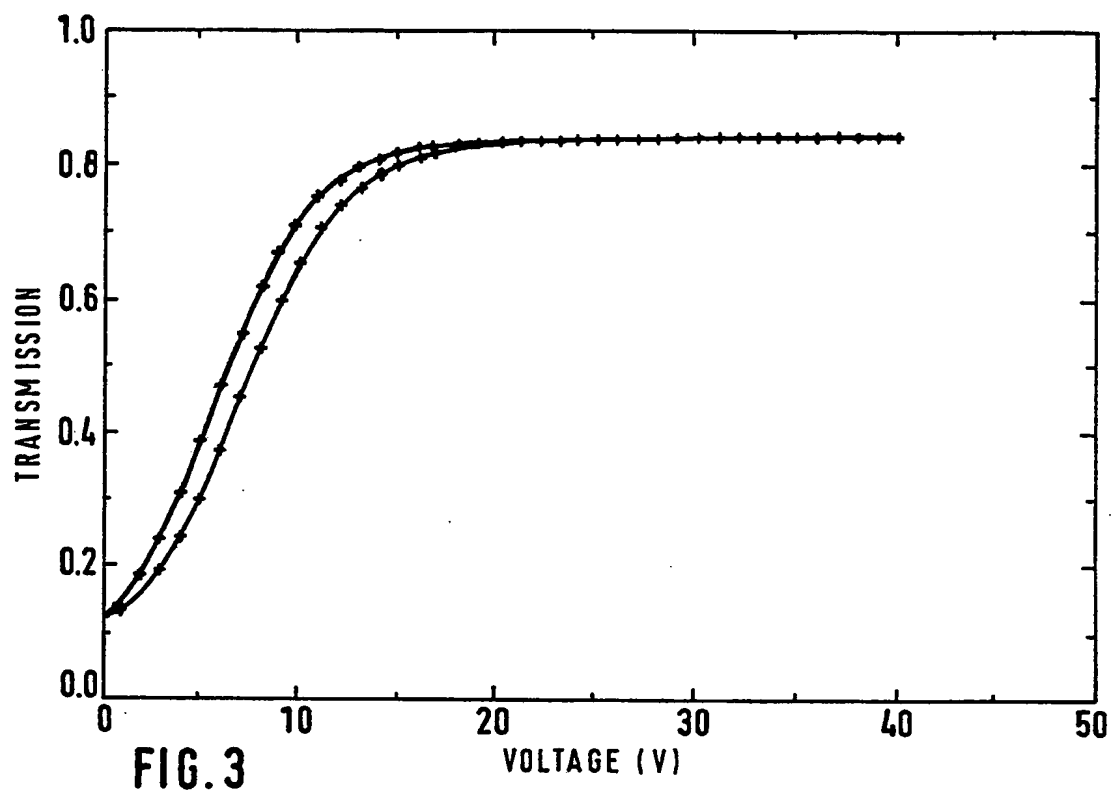
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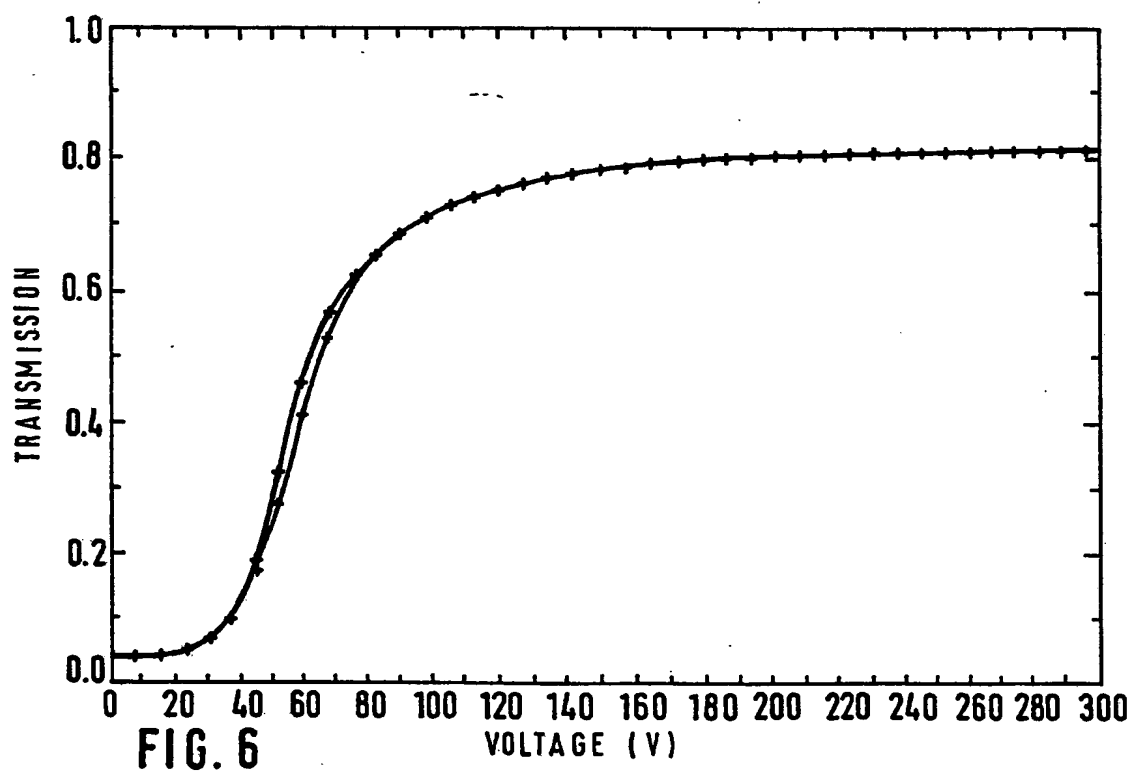
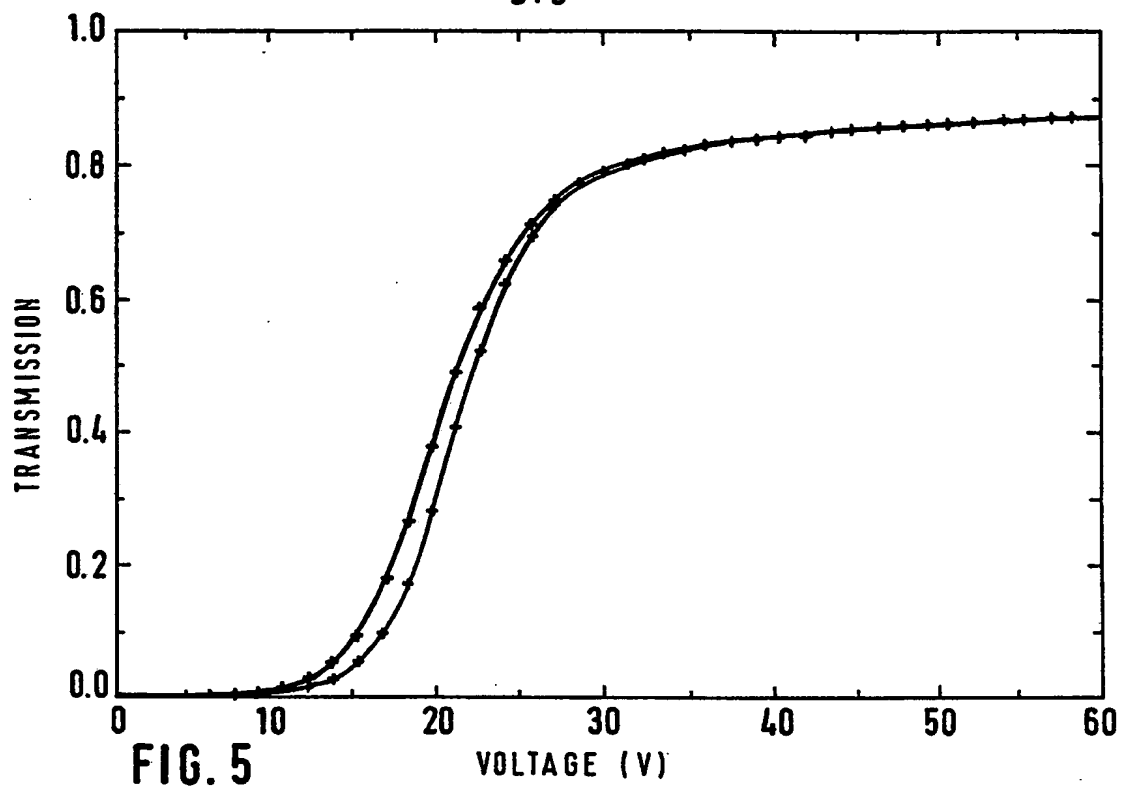
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3/3



INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/00989

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C09K19/54; C09K19/20;	G02F1/1333; C09K19/14;	C09K19/38; C09K19/12; C09K19/32 C09K19/34
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C09K ; G02F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X,P	EP,A,0 484 972 (CANON K.K.) 13 May 1992 see page 4, line 5 - line 9 see page 5, line 35 - page 10, line 48 see page 19 - page 24 see page 25, line 30 - page 31, line 44 see page 33, line 52 - page 34, line 25 ---	1-3,6-8
Y	WO,A,9 105 029 (MERCK) 18 April 1991 see page 1, line 1 - page 2, line 21 see example 1 see claims 1,7-14 ---	1,4-7
P,Y	DE,A,4 104 183 (MERCK) 30 July 1992 see page 3, line 22 - page 4, line 23 see page 15, line 40 - page 16, line 21 ---	1,4-7
-/--		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
30 JUNE 1993	05.06.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	BOULON A.F.J.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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P,X	see column 1, line 37 - column 2, line 19 see column 2, line 52 - column 3, line 28 see figures 1,2; examples 1-4	8
Y,P	EP,A,0 488 116 (SEIKO EPSON) 3 June 1992 see page 3, line 41 - page 5, line 2	1-3,6,7
Y	LIQUID CRYSTALS vol. 10, no. 6, December 1991, LONDON pages 835 - 847 R.A.M.HIKMET 'DIELECTRIC RELAXATION OF LIQUID CRYSTAL MOLECULES IN ANISOTROPIC CONFINMENTS'	1,2,5
X	see page 835 - page 836 see page 841 - page 847	8

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9300989
SA 73638

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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30/06/93.

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